4 itself. This result provides additional support for the hypothesis advanced to account for the dynamic NMR behavior of the more heavily substituted system. The close agreement between the calculated structure for **2** and that observed for **1** suggests that the substituents in the latter compound serve mainly to protect the reactive polysilane cage and do not strongly perturb its electronic structure. This analysis indicates that other calculations at this level of theory may be reliably used to predict the structure and properties of more strained polysilanes that have not yet yielded to synthesis. Further studies along these lines are in progress.

Parallel calculations on bicyclo[1.1.0]butane **4** suggest that the formal process of ring inversion entails rupture of the bridging bond and a barrier higher than that which opposes sigmatropic rearrangement to 1,3-butadiene.

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The Lowest Excited Triplet State of Triphenyl-, Diphenylchloro-, and Phenyldichlorocarbenium Ions and Their Isoelectronic Boron Compounds. An Optical and ODMR Spectroscopic Investigation Combined with MO Calculations

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Abstract: The lowest excited triplet states of triphenyl-, diphenylchloro-, and phenyldichlorocarbenium ions ($CPh_{3-m}Cl_m^+$) and of the respective isoelectronic boron compounds ($BPh_{3-m}Cl_m$) have been investigated by optical emission and ODMR spectroscopic methods in order to compare the triplet properties of the isoelectronic molecules in these two series as well as the change of triplet characteristics within each of the two series. The phosphorescence spectra, the triplet zero-field splitting parameters D and E, and the triplet spin sublevel selective deactivation rates were measured. Most of the experimental data were interpreted by an analysis of the triplet wave functions of these molecules in terms of intra-ring, inter-ring, charge-transfer ($Ph_{3-m} \rightarrow XCl_m$ ($X = B, C^+$)), and reverse-charge-transfer ($XCl_m \rightarrow Ph_{3-m}$) excitations. The wave functions were obtained by a π-SCF-CI-MO calculation. The carbenium ions showed low structured phosphorescence spectra, low-energy phosphorescence bands, and low D values whereas the boron compounds were characterized by well-structured phosphorescence spectra with typical benzenoid vibrational frequencies, high-energy 0-0 bands, and high D values. This indicates a non-benzene-like (delocalized) character of the T_1 states of the carbenium ions in contrast to a benzene-like (localized) character of the T_1 states of the boron compounds. This interpretation is in good agreement with the calculations which showed strong inter-ring and charge-transfer excitations with negligible intra-ring excitation for the carbenium ions and a strong increase of intra-ring excitation with a complementary decrease in inter-ring and charge-transfer excitations for the boron compounds. The correlation between experimental and calculational results is well reflected by the linear relationship between the measured D values and the calculated amount of intra-ring excitations. The variation of the T_1 properties of the molecules within each of the two series can be well explained by the lower electron-donating ability of the chlorine atoms as compared to the phenyl rings. The selective decay rates of the three triplet zero-field levels of all molecules investigated were analyzed in terms of the internal and external heavy-atom effect and the change of geometry.

1. Introduction

The physical and chemical properties of the organoboranes BR_3 and the isoelectronic carbenium ions CR_3^+ are of considerable interest. The isoelectronic structure of these compounds results in analogous chemical reactions. For example, the reaction with diazoalkanes[1] demonstrates the chemical similarity of BR_3 and CR_3^+. Furthermore, the analogous properties of BR_3 and CR_3^+ in the lower excited singlet states are expressed in the remarkable similarities of their UV spectra[2] and the response of the UV transitions to temperature changes.[3]

Although BR_3 and CR_3^+ are isoelectronic, important differences are encountered too in their physical properties due to the additional positive charge at C^+ in CR_3^+. An example constitutes the differing values for the ^{13}C chemical shifts for the para carbon atoms of the phenyl rings in BPh_3 and CPh_3^+.[4] Nevertheless, the correlations of the ^{13}C chemical shifts for the para carbon atoms[4] and for the $^{13}C^+$ and ^{11}B shifts[5] demonstrated the strong relationship between these isoelectronic compounds.

So far, correlations between the isoelectronic boron and carbenium compounds were restricted to the ground state S_0 and excited singlet states. Therefore, we started investigations[6] to compare the properties of the lowest triplet state T_1 of BPh_3 and CPh_3^+ by means of ODMR (optical detection of magnetic resonance) and optical luminescence spectroscopies, which represent the most appropriate techniques.

The chemical and physical properties of BR_3 and CR_3^+ are governed by the ability of the substituents R to compensate the

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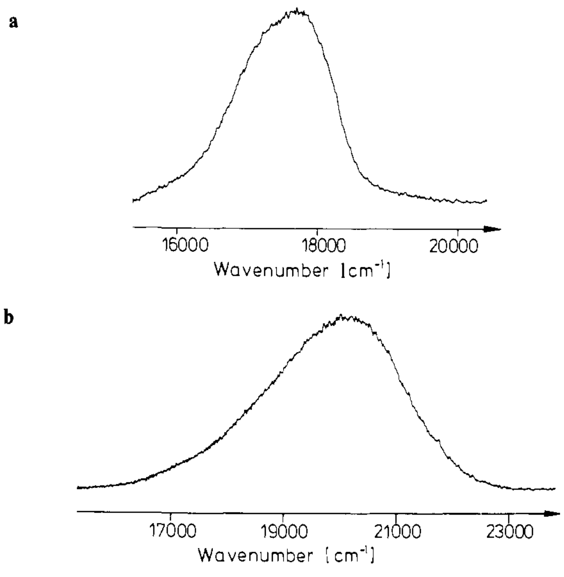

Figure 1. (a) The phosphorescence spectrum of $CPh_2Cl^+/SbCl_6^-$ in CH_2Cl_2 at 4.2 K. (b) The phosphorescence spectrum of $CPhCl_2^+/SbCl_6^-$ in CH_2Cl_2 at 4.2 K.

electron deficiency of the empty p_π-orbital at the atom X (X = B, C^+) via conjugative and inductive effects.[7-13] Phenyl rings constitute good electron-donating groups whereas chlorine substituents are less effective.[12,14] Therefore we extended our investigations of the isoelectronic pair, triphenylcarbenium ion CPh_3^+ and triphenylborane BPh_3, by the study of the pairs diphenylchlorocarbenium ion CPh_2Cl^+ and diphenylchloroborane BPh_2Cl, as well as phenyldichlorocarbenium ion $CPhCl_2^+$ and phenyldichloroborane $BPhCl_2$.

The series $CPh_{3-m}Cl_m^+$ and $BPh_{3-m}Cl_m$ with m = 0, 1, and 2 allow the correlation of properties of the T_1 state between isoelectronic pairs and an assessment of the variations of the electronic structures due to the successive replacement of phenyl rings by chlorine substituents. In this paper we want to present the combined results and a comparison of the T_1 state properties of $XPh_{3-m}Cl_m$. Therefore the new experimental results on $CPh_2Cl^+/SbCl_6^-$, BPh_2Cl, and $CPhCl_2^+/SbCl_6^-$ in section 2.1 are supplemented by our preliminary published data on $CPh_3^+/SbCl_6^-$, BPh_3,[6] and $BPhCl_2$.[15]

Various theoretical investigations[2,8-11,16] showed that charge transfer (CT), i.e., the electron donating from the substituents R to the central atom X, is important for the properties of the S_0 state as well as of the $S_0 \rightarrow S_1$ transition in CR_3^+ and BR_3, however, to the best of our knowledge no detailed theoretical studies have been reported for all of the three isoelectronic pairs. Therefore we supplemented our experimental work by MO calculations in order to elucidate the electronic structures of $CPh_{3-m}Cl_m^+$ and $BPh_{3-m}Cl_m$ in singlet ground and triplet excited states. In section 2.2 the MO calculations are described and their results are given. The combined discussion of experimental and numerical results is carried out in section 3.

2. Results

2.1. Experimental Results. In this paper we want to compare both the carbenium ions with their isoelectronic compounds and the systems within these series. Thus the new results for CPh_2Cl^+, BPh_2Cl, and $CPhCl_2^+$ are supplemented by the values for CPh_3^+, BPh_3, and $BPhCl_2$ from the preliminary work of our group.[6,15] We want to mention that all compounds were measured in CH_2Cl_2 except $BPhCl_2$, which was dissolved in n-hexane.

The absorption spectra of $CPh_2Cl^+/SbCl_6^-$ and $CPhCl_2^+/SbCl_6^-$ were recorded at room temperature and are in accordance with those of the literature.[12,17-19] The phosphorescence spectra at

Table I. λ_{max} and λ_{0-0} Values, Respectively, Experimental ZFS Parameters D and E, and the Amount z of the Intra-Ring Excitation for the Lowest T_1 State of the Carbenium and Boron Compounds

	λ_{max}, nm	$\|E\|$, MHz	$\|D\|$, MHz	z, %
$CPh_3^+/SbCl_6^-$[a]	546	434	1965	0[c]
$CPh_2Cl^+/SbCl_6^-$	562	394	2044	0[c]
$CPhCl_2^+/SbCl_6^-$	497	504	2714	34[c]
	λ_{0-0}, nm	$\|E\|$, MHz	$\|D\|$, MHz	z, %
BPh_3[a]	382	242	2912	48[d]
BPh_2Cl	383	305	3089	57[d]
$BPhCl_2$[b]	380	163	3602	85[c]

[a] From ref 6. [b] From ref 15. [c] Estimated from x and y values and from analysis of the wave functions. [d] Estimated from Figure 5.

Table II. Total Decay Rates of the ZFLs of the Carbenium and Boron Compounds in Different Solvents[d]

compd (solvent)	k_1, 1/s ($\|D\| + \|E\|$)	k_2, 1/s ($\|D\| - \|E\|$)	k_3, 1/s ($\|D\| + \|E\|$), ($\|D\| - \|E\|$)
$CPh_3^+/SbCl_6^-$[a] (CH_2Cl_2)	20.86	11.76	3.45
$CPh_2Cl^+/SbCl_6^-$ (CH_2Cl_2)	14.38	24.40	2.93
$CPhCl_2^+/SbCl_6^-$ (CH_2Cl_2)	17.22	33.74	3.14
BPh_3 (CH_2Cl_2)[a]	15.39	13.70	1.28
BPh_3 (n-octane)[a]	8.56	10.35	0.48
BPh_2Cl (CH_2Cl_2)	10.00	11.11	0.96
$BPhCl_2$ (n-hexane)[b]	3.98	4.09	0.40
PBC (n-hexane)[c]	0.33	0.22	0.085

[a] From ref 6. [b] From ref 15. [c] From ref 24. [d] ODMR transitions from which the rates were obtained are indicated at the top of the table.

Table III. Vibrational Analysis of the Phosphorescence Spectrum of BPh_2Cl in CH_2Cl_2

intensity	λ_E, nm	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	assignment
w	382.7	26 128		0–0 band
m	389.6	25 668	460 (400)	ν_{16}'
m	392.4	25 481	647 (631)	ν_6'
m	398.1	25 117	1011 (998)	ν_1'
s	401.3	24 920	1208 (1187)	ν_9'
vs	407.4	24 545	1583 (1593)	ν_8'
vs	416.1	24 035	2093	$\nu_{16}' + \nu_8'$
vs	434.6	23 010	3118	$2\nu_8'$

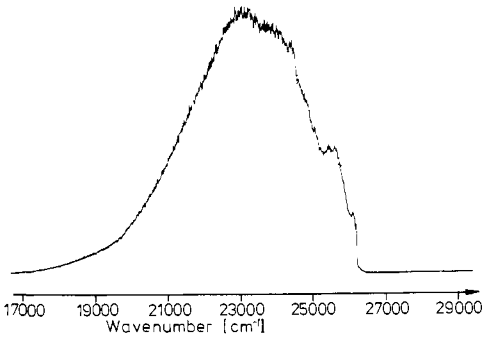

Figure 2. The phosphorescence spectrum of BPh_2Cl in CH_2Cl_2 at 1.5 K.

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Table IV. Parameters for the π-SCF Calculations: Core Energies U, One-Center Coulomb Integrals γ, Resonance Integrals β, and Bond Lengths r

atom	U, eV	γ, eV	β, eV	bond	r, pm
C	−11.16	9.76	−2.33	C−C	140
B	−1.06	5.97	−2.09	C−Ph	146[a]
Cl	−23.40	10.04	−1.22	B−C	157.7[b]
			−1.22	B−Cl	174[c]
			−1.22	C−Cl	172[d]

[a] Cf. *x*-ray analysis[28] of CPh_3^+/ClO_4^-. [b] Mean value in X-ray analysis[27] of BPh_3. [c] Cf. ref 51. [d] Mean value of bond lengths in CCl_4 and PhCl, cf. ref 51.

4.2 K are shown in Figure 1a and 1b. Both spectra contain a broad band indicating a strong phonon coupling. The positions of the maximum intensity of the phosphorescence (λ_{max}) are given in Table I. The zero-field splitting (ZFS) parameters D and E of the carbenium ions are summarized in Table I. The total decay rates of the three zero-field levels (ZFL) of T_1 were determined by MIDP measurements.[20] The results are listed in Table II.

The phosphorescence spectrum of BPh_2Cl at 1.5 K is shown in Figure 2. The vibrational analysis is given in Table III. The assignment of the vibronic bands is based on the normal vibrational modes of benzene,[21] $\upsilon_1 = 992$, $\upsilon_6 = 605$, $\upsilon_8 = 1584$, $\upsilon_9 = 1178$, and $\upsilon_{16} = 404$ cm^{-1}, by utilizing Wilson's numbering.[22] The wavenumbers of the corresponding vibrations from IR measurements of BPh_2Cl[23] are added in brackets in Table III. All the experimental data for the boron compounds are added to the corresponding values of the carbenium ions in Tables I and II. Furthermore, we included in Table II the total decay rates of BPh_3 in *n*-octane and of 1-phenyl-1-boracyclohexane (PBC)[24] for reasons discussed in section 3. It should be mentioned that the total decay rates for BPh_3 in *n*-octane (cf. Table II) differ slightly from those published earlier[6] since they were determined by the more accurate MIDP experiments.[20]

2.2. Calculational Results. The size of the compounds of interest prevents the application of ab initio methods, and so a semiempirical approach had to be used, which on the other hand facilitates the interpretation of the numerical results. The wave functions for the ground state S_0 and the triplet states are obtained by a π-SCF calculation with subsequent configuration interaction between all singly excited configurations. The utilized core energies, resonance integrals, and one-center Coulomb integrals were chosen similar to those in 9–11,25 and are collected in Table IV. The two-center Coulomb integrals were calculated with the Mataga–Nishimoto formula.[26] Torsions between the central atom X = B and C^+ and the phenyl rings are taken into account by a factor cos θ in the resonance integrals where θ denotes the torsion angle.

Idealized geometries were used in the calculations with planar phenyl rings, and the bond lengths given in Table IV. Following the results of X-ray analyses for BPh_3 and CPh_3^+/ClO_4^-,[27,28] a torsion angle $\theta = 30°$ and $32°$ was used for these compounds as well as for BPh_2Cl and CPh_2Cl^+. For the latter two isoelectronic systems the calculations were repeated with $\theta = 5°$. $BPhCl_2$ and $CPhCl_2^+$ were assumed to be planar.

The results of our calculations for the molecules $XPh_{3-m}Cl_m$ are collected in Table V. There the net charges q_X^0 and $q_{XCl_m}^0$ on X and XCl_m (a negative value denotes excess electron density) in the ground state S_0 as well as the coresponding values q_X and q_{XCl_m} in the triplet state T_i of interest are given together with the triplet excitation energies T for transitions $S_0 \rightarrow T_i$. The triplet states are analyzed in terms of predominant configurations $\phi_i \rightarrow \phi_k$ with a one-electron transition from the occupied orbital ϕ_i into the virtual one ϕ_k. Futhermore, x and y values are given which denote the percentage of the excitation out of the XCl_m group and into the XCl_m group.

Although the calculated T values are smaller by 0.3–0.4 eV than the experimental ones, they reflect correctly the difference between the two series $BPh_{3-m}Cl_m$ and $CPh_{3-m}Cl_m^+$, i.e., the constant value of T for the boron compounds and the variation of T in the carbenium ion series. Furthermore, Table V reveals that T as well as the other ground- and triplet-state properties of BPh_2Cl and CPh_2Cl^+ do not depend significantly on the size of the torsion angle between the phenyl rings and the XCl group, similar to the case of BPh_3[9] and CPh_3^+.[29] Consequently, inadequacies in the geometries used in our calculations are insignificant for a discussion of the electronic properties of the studied systems. On the other hand, for the same reason our theoretical and experimental results cannot contribute to the often discussed problem of the geometry, i.e., the torsion angles between phenyl rings and the central atom X = B and C^+, of these molecules in ground and excited states in solution or solid state.

For $BPh_{3-m}Cl_m$ with m = 1 and 2 and CPh_3^+, the lowest two triplet states are degenerate, for BPh_3 even the lowest three states are (nearly) degenerate. We do not know which of these degenerate states represents the T_1 state in solid solution; i.e., which state is stabilized more than the others by field effects and symmetry reduction. However, this turns out to be unimportant for our discussion since all the degenerate states exhibit quite similar triplet-state properties as is demonstrated in Table V. This applies as well to the ZFS parameters since a coupling between the degenerate states is impossible.[30]

3. Discussion

In both series $CPh_{3-m}Cl_m^+$ and $BPh_{3-m}Cl_m$, the central atom (C^+ and B, respectively) is characterized by an electron deficiency due to the empty p_π-orbital.[31] It therefore withdraws electrons from the substituents, i.e., from the phenyl ring(s) and the chlorine atom(s). Calculated charge densities[9-11] for the boron compounds and also various investigations of the carbenium ions[2,4,7,12,16] indeed indicate the charge transfer (CT) to the central atom C^+ or B in the singlet ground state S_0. Our calculated charge densities q_X^0 in Table V agree with these findings. As expected, the CT in S_0 is greater in the case of the carbenium ions (~0.4 elementary charge) than for the boron compounds (~0.1 elementary charge) due to the positively charged carbon atom in $CPh_{3-m}Cl_m^+$. For the triplet states a corresponding difference between the two series follows immediately from the slightly negative charge densities q_X (more than one electron is transferred to the central carbon atom) for the carbenium ions as compared to the quite small values of q_X for the boron compounds.

In our work we want to compare the CT character of the T_1 state of the carbenium and boron compounds. For this purpose the degree of the localization of the T_1 wave function in the phenyl ring(s) or of its delocalization throughout the whole molecule has to be determined. Informations about the (de)localization of T_1 are derived from both the experimental and calculational results.

In the studied compounds four different types of excitations in T_1 have to be considered: (a) an excitation within the phenyl ring(s) (intra-ring excitation), (b) an excitation between different

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Table V. Data for the Lowest Triplet States of $BPh_{3-m}Cl_m$ and $CPh_{3-m}Cl_m^+$ Derived from MO Calculations[e]

compd	T, eV	T_{exp},[a] eV	$\phi_i \rightarrow \phi_k$	(%)	x, %	y, %	q_X^0	q_X	$q_{XCl_m}^0$	q_{XCl_m}
BPh_3[b]	2.8	3.2	9 → 10	(14.9)	0.4	7.1	−0.07	−0.14		
	2.8		8 → 10	(14.9)	0.4	7.1		−0.14		
	2.8		9 → 14	(15.5)	0.5	6.2		−0.13		
			8 → 15	(15.5)						
BPh_2Cl[b]	2.8	3.2	7 → 8	(24.6)	1.4	8.7	−0.08	−0.16	−0.04	−0.12
	2.8		7 → 11	(23.2)	1.5	8.1		−0.16		−0.11
BPh_2Cl[c]	2.8	3.2	7 → 8	(25.8)	1.4	9.3	−0.09	−0.18	−0.05	−0.13
	2.8		7 → 11	(23.2)	1.6	8.4		−0.17		−0.12
$BPhCl_2$	2.8	3.2	5 → 7	(44.8)	3.8	12.7	−0.10	−0.22	−0.03	−0.12
			4 → 6	(44.8)						
CPh_3^+[d]	2.0	2.3	9 → 10	(83.1)	0.3	40.1	+0.35	−0.04		
	2.0		8 → 10	(83.1)	0.3	40.1		−0.04		
CPh_2Cl^+[d]	1.9	2.2	7 → 8	(87.0)	0.9	51.5	+0.40	−0.06	+0.52	+0.02
CPh_2Cl^+[c]	2.0	2.2	7 → 8	(86.4)	1.0	44.5	+0.36	−0.04	+0.47	+0.03
$CPhCl_2^+$	2.1	2.5	5 → 6	(94.1)	0.4	62.9	+0.43	−0.09	+0.68	+0.05

[a] Calculated from λ_{0-0} and λ_{max}, respectively, in Table I. [b] Torsion angle $\theta = 30°$. [c] $\theta = 5°$. [d] $\theta = 32°$. [e] T is the triplet excitation energy and T_{exp} the corresponding experimental value (λ_{0-0} and λ_{max}, respectively). Analysis of the triplet wave function in terms of x (excitation out of XCl_m) and y (excitation into XCl_m) and predominant configurations $\phi_i \rightarrow \phi_k$. In the last column net charges q_X^0, $q_{XCl_m}^0$, q_X, and q_{XCl_m} for ground and excited triplet states are given.

phenyl rings (inter-ring excitation), (c) charge-transfer excitation $Ph_{3-m} \rightarrow XCl_m$, and (d) reverse-charge-transfer excitation $XCl_m \rightarrow Ph_{3-m}$.

First information about the excitation patterns can be gained from the x and y values given in Table V. For all studied compounds the x values are small. Consequently, a reverse CT is insignificant in the lowets triplet states. On the other hand, the excitation into the XCl_m group (cf. y values) is significant in the boron compounds (6–13%) and even more important in the carbenium ions (40–63%) which corresponds to the greater CT character of T_1 for the latter as revealed by the charge distributions. We will show below the way in which more information on the excitation pattern in T_1 can be obtained by inspection of x and y values and the analysis of the wave functions for the isoelectronic pairs.

3.1. Comparison between CPh_3^+ and BPh_3. A detailed discussion of the experimental results for CPh_3^+ and BPh_3 was given in ref 6. According to ref 6, BPh_3 showed a strong benzene-like behavior, and a triplet wave function which is strongly localized in the phenyl rings has to be assumed. On the contrary, CPh_3^+ was not characterized by benzene-like behavior, but a strong electron delocalization in T_1 was indicated. This result and interpretation derived from experimental measurements have to be compared with the T_1 wave function calculated in section 2.2.

Figure 3 demonstrates the difficulty of using only the x and y values for evaluating the amounts of intra- or inter-ring excitation in T_1 of CPh_3^+. For example, we can assign 19.9% of excitation in T_1 either only to inter-ring (Figure 3a) or only to intra-ring (Figure 3b) excitation. Thus for evaluating the exact amount of the different excitation types a more detailed analysis of the T_1 wave function is necessary.

The lowest T_1 state of CPh_3^+ is doubly degenerate; however, both states exhibit the same character, and we need to discuss only one of them, which is given as (Table V)

$$(\phi_8 \rightarrow \phi_{10}) \simeq 0.47\{(\phi_3^b \rightarrow \phi_C) - (\phi_3^c \rightarrow \phi_C)\} + \\ 0.37\{(\phi_3^b \rightarrow \phi_3^a) + (\phi_3^b \rightarrow \phi_3^c) - (\phi_3^c \rightarrow \phi_3^a) - (\phi_3^c - \phi_3^b)\}$$

if we neglect the small mixing of the predominant configurations with others. Here ϕ_i^a, ϕ_i^b, and ϕ_i^c represent the MOs at the benzene rings a, b, and c, whereas ϕ_C means the p_π-orbital at the atom C^+. The analysis of this wave function shows that in CPh_3^+ 44.9% CT and 55% inter-ring excitation contribute to T_1. Similar values for the excitation pattern are obtained from the complete wave function. This analysis reveals that no significant intra-ring excitation which would signify "pure" benzene character in T_1 is encountered in CPh_3^+.

An analogous numerical analysis of T_1 for BPh_3 is impossible because the lowest (almost) degenerate triplet states consist of many different configurations with similar weight. Therefore only qualitative considerations can be carried out for BPh_3 which, however, will give us additional important insight into the characteristic difference between the isoelectronic CPh_3^+ and BPh_3.

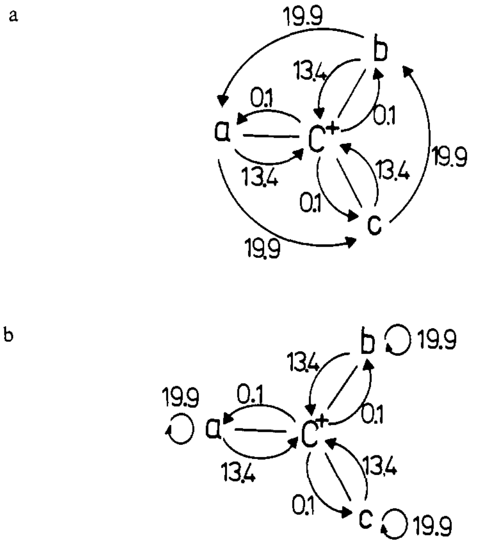

Figure 3. Two possible excitation patterns (in %) in T_1 of CPh_3^+ derived from x and y values. The phenyl rings are denoted by a, b, and c, the inter-ring excitations by the arrows between a, b, and c. The intra-ring excitations are denoted by the arrows at a, b, and c, and the CT as well as reverse CT excitations by the arrows between the phenyl rings and central atoms.

We form symmetry-adapted functions within the symmetry point group C_3 which is appropriate for XPh_3 in the following way:

$$\phi_i^1 = 3^{-1/2}(\phi_i^a + \phi_i^b + \phi_i^c)$$

$$\phi_i^2 = 2^{-1/2}(\phi_i^b - \phi_i^c)$$

$$\phi_i^3 = (2\phi_i^a - \phi_i^b - \phi_i^c)$$

Now we allow in BPh_3 mixing of the symmetry-adapted functions with the AO ϕ_B at boron. The resulting MO pattern is shown in Figure 4. Applying the same procedure to CPh_3^+ with the symmetry-adapted phenyl functions and the AO ϕ_C at C^+, we arrive at a similar MO pattern for CPh_3^+ (see Figure 4), however, with a LUMO (ϕ_{10}) at a much lower energy. This is due to the different core energies of B and C^+, Table IV. The MO patterns also rationalize that the lowest triplet states of CPh_3^+ are dominated by the $\phi_{8,9} \rightarrow \phi_{10}$ transitions whereas many configurations mix in the case of BPh_3. An analysis of x and y values in Table V demonstrates that there are considerable amounts of inter *and* intra-ring excitations besides a small contribution of CT excitation for BPh_3. As we have shown, only CT and inter-ring excitations occur in T_1 of CPh_3^+. Since the portion of intra-ring excitation contributing to T_1 is a measure for the benzene-like (localized)

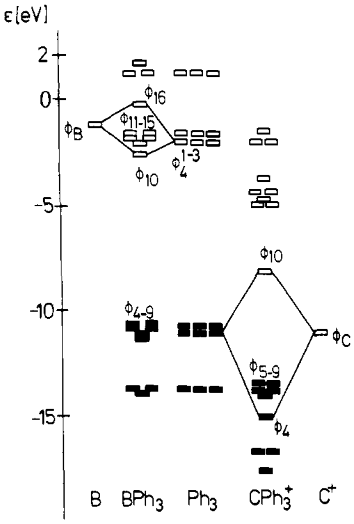

Figure 4. Orbital energies ϵ and occupation schemes for BPh_3 ($\theta = 30°$), CPh_3^+ ($\theta = 32°$), and the corresponding subsystems B, C^+, and Ph_3. Black bars denote occupied and white bars virtual orbitals.

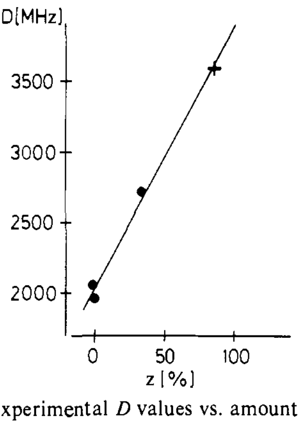

Figure 5. Plot of experimental D values vs. amount z of intra-ring excitations in the lowest triplet states of $CPh_{3-m}Cl_m^+$ with m = 0, 1, and 2 (●) and $BPhCl_2$ (+).

character of the T_1 wave function, we summarize in Table I the amounts of intra-ring excitation (z). As the D value for these molecules can be interpreted in first order as a measure of the contribution of localized benzene rings to T_1, we expect a correlation between the D parameters and the x values. Figure 5 shows such a plot. The linear relationship between the measured D values and the calculated z values enables us to infer from this plot z = 48% for BPh_3.

Our calculations are in good agreement with the conclusions deduced earlier from experiments about the T_1 character of CPh_3^+ and BPh_3. The large amount of intra-ring excitation in BPh_3 and the negligible one in CPh_3^+ correlates very well with the deduced benzene-like (localized) character of the T_1 state of BPh_3 and the non-benzene-like (delocalized) character of CPh_3^+.

3.2. Comparison between CPh_2Cl^+ and BPh_2Cl. Information about the CT character and thus about the delocalization of electrons in the T_1 state of these two molecules comes from both our experiments and our calculations. As for the pair CPh_3^+ and BPh_3 discussed above, already the observed phosphorescence spectra of CPh_2Cl^+ and BPh_2Cl allow conclusions on the nature of the T_1 states.

CPh_2Cl^+ shows a very broad phosphorescence band and a low-energy λ_{max} position as compared to benzene.[33] The broad band results from strong electron phonon coupling normally accompanying a strong CT transition.[34] Furthermore, no specific benzenoid vibrations occur in the phosphorescence spectrum. These characteristics of the phosphorescence spectrum indicate that the radiative deactivation of T_1 of CPh_2Cl^+ proceeds in a completely different way as compared to the (localized) T_1 state of benzene.[33] Thus the T_1 wave function of CPh_2Cl^+ is assumed to be delocalized throughout the *whole* molecule.

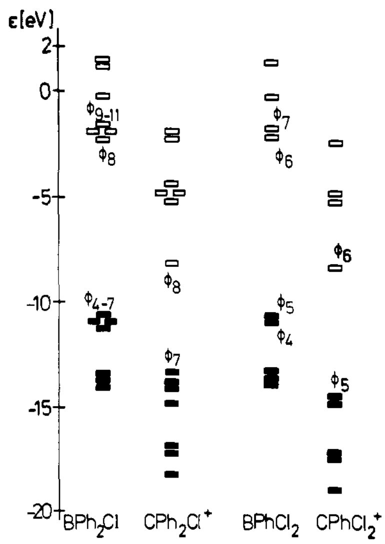

Figure 6. Orbital energies ϵ and occupation schemes for BPh_2Cl, CPh_2Cl^+, $BPhCl_2$, and $CPhCl_2^+$. Black bars denote occupied and white bars virtual orbitals.

In contrast to CPh_2Cl^+ the isoelectronic BPh_2Cl shows a benzene-like phosphorescence spectrum: the 0–0 band is very weak and only benzenoid vibrations occur in the spectrum. From these facts it is obvious that the T_1 wave function of BPh_2Cl possesses a strong benzoid character, i.e., is strongly localized on the phenyl rings.

Further information about the CT character in T_1 of the isoelectronic CPh_2Cl^+ and BPh_2Cl comes from the D values given in Table I. The D parameter of CPh_2Cl^+ is extremely small (D = 2044 MHz) compared with other substituted benzene systems showing values typically between 3000 and 4000 MHz.[24,35–38] This can be explained by a strong delocalization of the T_1 wave function and hence a strong CT character in this carbenium ion. This is in accordance with the phosphorescence behavior. The considerably higher D value and the observed phosphorescence for BPh_2Cl indicates a relatively small CT character and a benzene-like T_1 wave function. In order to obtain more detailed information on the character of the T_1 excitation of CPh_2Cl^+ and BPh_2Cl we again have to analyze the calculated T_1 wave functions.

The analysis of the lowest wave function for CPh_2Cl^+ proceeds in the same manner as for CPh_3^+. The predominant configuration in the T_1 wave function of CPh_2Cl^+ is the excitation $\phi_7 \rightarrow \phi_8$, which is to be expected from the MO scheme shown in Figure 6. Neglecting the small mixing of this configuration with others, we arrive at the following for the T_1 wave function.

$$\begin{aligned}(\phi_7 \rightarrow \phi_8) \simeq\ & 0.51\{(\phi_3^a \rightarrow \phi_C) - (\phi_3^b \rightarrow \phi_C)\} - \\ & 0.46\{(\phi_3^a \rightarrow \phi_3^b) - (\phi_3^b \rightarrow \phi_3^a)\} - \\ & 0.16\{(\phi_3^a \rightarrow \phi_{Cl}) - (\phi_3^b \rightarrow \phi_{Cl})\}\end{aligned}$$

Again the analysis of the $\phi_7 \rightarrow \phi_8$ configuration for the carbenium ion yields mainly a CT excitation from the phenyl rings to the central C^+ and inter-ring excitations. For the complete T_1 wave function for CPh_2Cl^+ we calculated about 51% CT and 49% inter-ring excitations, but *no* intra-ring excitations are present significantly in T_1. This result is in agreement with our exper-

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imental findings that T_1 is delocalized over the phenyl rings *and* the central C^+.

Similar to BPh_3 many configurations mix in the lowest triplet states of BPh_2Cl which can be rationalized from the MO scheme for BPh_2Cl in Figure 6. A similar qualitative analysis of T_1 for BPh_2Cl as for BPh_3 reveals that intra- *and* inter-ring excitations are dominating in T_1. Using the plot in Figure 5 we derive a value of about 57% for the amount of intra-ring excitation in T_1 of BPh_2Cl. This high value for the intra-ring excitation is in good agreement with the experimental findings, i.e., the relatively high D parameter and the phosphorescence properties. Thus BPh_2Cl shows a strong benzene-like behavior in its T_1 wave function which is mainly localized on the phenyl rings.

3.3. Comparison between $CPhCl_2^+$ and $BPhCl_2$. The experimental results for $BPhCl_2$ were discussed in ref 15. Since $BPhCl_2$ was investigated in *n*-hexane, a highly resolved phosphorescence spectrum was observed due to the Shpol'skii effect.[40] It was shown that the radiative decay of T_1 is similar to that of benzene.[15] A comparison between the spectra and D values of $CPhCl_2^+$ and $BPhCl_2$ again demonstrates the completely different characters of the T_1 states of the two isoelectronic compounds. Since the different characters of T_1 for $CPhCl_2^+$ and $BPhCl_2$ are expressed by the experimental results in the same way as for CPh_2Cl^+ and BPh_2Cl discussed above, we give only a short summary of these findings.

The broad phosphorescence band, the low-energy λ_{max} value, the absence of benzenoid vibrations in the phosphorescence spectrum, and the low D value again demonstrate a nonbenzenoid character for the T_1 state of $CPhCl_2^+$. However, in contrast $BPhCl_2$ possesses a benzene-like T_1 state following from the weak 0–0 band, the dominating ν_8 benzenoid vibration (Wilson's numbering[22]), and the quite large D value. Furthermore, the highly resolved phosphorescence spectrum of $BPhCl_2$ resembles those of such substituted benzene compounds as toluene,[41] which are not characterized by CT character. Thus the experimental results indicate a high degree of CT character in the T_1 wave function of $CPhCl_2^+$ and a strong electron delocalization. In contrast the CT character and thus the electron delocalization in T_1 of $BPhCl_2$ appear to be considerably smaller.

Since $CPhCl_2^+$ and $BPhCl_2$ contain only one phenyl ring, no inter-ring excitation is possible. Thus the x and y values in Table V yield directly the possible magnitudes of intra-ring and CT excitations. For $BPhCl_2$ between 83.5% and 87.3% of the T_1 wave function consists of intra-ring excitation whereas most of the rest has to be attributed to a CT excitation from the phenyl ring to the boron atom (8.9–12.7%). This provides a more accurate estimate of the CT character in T_1 of $BPhCl_2$ than that in our previous work[15] where a relation derived by Godfrey et al.[42] was used. For $CPhCl_2^+$ the x and y values lead to the conclusion that only 36.7–37.1% of the T_1 wave function describe an intra-ring excitation whereas 62.5–62.9% has to be attributed to the CT excitation. The character of the T_1 wave function for $BPhCl_2$ and $CPhCl_2$ agrees well with the experimental findings.

The MO schemes for $BPhCl_2$ and $CPhCl_2^+$ in Figure 6 show similar characteristic features as those for BPh_2Cl and CPh_2Cl^+ in Figure 6 and BPh_3 and CPh_3^+ in Figure 4; i.e., only the carbenium ion possesses a low-lying LUMO. Therefore the T_1 wave function of $CPhCl_2^+$ is dominated by the $\phi_5 \rightarrow \phi_6$ configuration whereas the near degeneracy of the highest occupied ($\phi_{4,5}$) and the lowest virtual ($\phi_{6,7}$) orbitals leads to the mixing of the two configurations $\phi_4 \rightarrow \phi_6$ and $\phi_5 \rightarrow \phi_7$ in $BPhCl_2$.

3.4. Variation of T_1 Properties within the Series $CPh_{3-m}Cl_m^+$ and $BPh_{3-m}Cl_m$. The comparison of each pair of isoelectronic compounds will be completed by a general survey of the variation of the T_1 character within the series $CPh_{3-m}Cl_m^+$ and $BPh_{3-m}Cl_m$. Since the substituents at the central atom X serve as electron donors, we expect some characteristic changes for T_1 in these two series when substituting the phenyl ring(s) by the chlorine atom(s) according to their different electron-donor ability.

In the ground state the different electron-donor property is demonstrated by the well-known decreasing stability of the carbenium ions $CPh_{3-m}Cl_m^+$ when substituting the phenyl ring(s) by the chlorine atom(s).[12,14] Thus in S_0 the positive charge is better stabilized by a phenyl ring than by a chlorine atom. The increase of our calculated positive charge density $q_X{}^0$ at C^+ in S_0 within the series $CPh_{3-m}Cl_m^+$ is in accordance with the observed decreasing stability. In contrast the charge density $q_X{}^0$ in the series $BPh_{3-m}Cl_m$ is numerically small and nearly constant when substituting the phenyl ring(s) by chlorine atom(s). The reason for the larger $q_X{}^0$ and thus the larger electron transfer in S_0 for $CPh_{3-m}Cl_m^+$ than for $BPh_{3-m}Cl_m$ follows immediately from the MO patterns in Figures 4 and 6. For the carbenium ions the AO ϕ_C at C^+ is mixed together with a bonding MO of the Ph_{3-m} group producing a considerable population of ϕ_C in S_0, whereas for the boron compounds the AO ϕ_B at B is mixed only slightly with higher virtual MOs of the Ph_{3-m} group yielding a negligible population of ϕ_B in S_0.

The amount of charge delocalization for the carbenium ions changes dramatically in the T_1 states when compared with the S_0 states. The charge density q_X in T_1 is even negative and increases with m in the series $CPh_{3-m}Cl_m^+$. Nearly no difference of the charge densities between the T_1 and S_0 states is found for the boron compounds. This different behavior of carbenium and boron compounds is rationalized by the considerably larger CT character of the T_1 excitation for the $CPh_{3-m}Cl_m^+$ ions with respect to the isoelectronic $BPh_{3-m}Cl_m$ molecules.

The small electron-donating power of the chlorine atom(s) in T_1 for both series is not only demonstrated by the small differences between the q_X and q_{XCl_m} values but also by the established negligible excitation within the XCl_m group in T_1 for all compounds containing chlorine atom(s). Thus the properties of T_1 in these series will be governed by CT from the phenyl ring(s) to the central atom or by the amount (z) of intra-ring excitation. Our calculated z values indeed yielded a good correlation with the measured D parameters.

The first substitution of a phenyl ring by a chlorine atom in both series does not alter considerably the character of the T_1 states since the two molecules CPh_3^+ and CPh_2Cl^+ as well as BPh_3 and BPh_2Cl each possess similar D and z values. From these results we conclude that the two phenyl rings in CPh_2Cl^+ and BPh_2Cl produce an equivalent charge delocalization as the three phenyl rings in CPh_3^+ and BPh_3. This is in accordance with the quite similar z values indicating a lower amount of intra-ring excitation per *one* ring in CPh_3^+ and BPh_3, respectively, with respect to CPh_2Cl^+ or BPh_2Cl.

A considerable change of the two values D and z is observed for the third molecule in these series: $CPhCl_2^+$ and $BPhCl_2$. Due to the increase of the intra-ring excitation value z, the T_1 wave function contains more benzene-like character and thus the D values for $CPhCl_2^+$ and $BPhCl_2$ become larger. In $CPhCl_2^+$ and $BPhCl_2$ CT from only *one* phenyl ring to the central atom X takes place, and in addition no inter-ring excitation between different phenyl rings can contribute to T_1. Consequently, the amount of intra-ring excitation z in T_1 for $CPhCl_2^+$ and $BPhCl_2$ exceeds those of the other compounds in each of the series, and the D values increase.

The variation of the λ_{max} values for the carbenium ions parallels the behavior of the z and D values. However, the λ_{0-0} values for the boron compounds do not nearly change in contrast to the D and z values. The constancy of λ_{0-0} and the calculated T values is due to the relatively small CT character in the T_1 state of the boron compounds.

3.5. T_1 Zero-Field Level Selective Decay Rates. Finally, some comments shall be made to the total decay rates of the three ZFLs summarized in Table II. We first assume that the triplet states possess mainly $\pi\pi^*$ character since excitation occurs within the π-electron system of the phenyl ring(s) and the p_π-orbital at X. Although $CPh_{3-m}Cl_m^+$ and $BPh_{3-m}Cl_m$ with $m = 0$ and 1 cannot

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be planar, the well-known ordering $k_1 \cong k_2 \triangleq k_{\text{in-plane}} > k_3 \triangleq k_{\text{out-of-plane}}$ of the rates of aromatic molecules[43] is still found for all compounds. Thus the deviations from a planar geometry in these compounds are not large enough to reduce considerably the separation of the in-plane and out-of-plane rates.

Comparing the total decay rates of the compounds, we have to take into account three effects[33] influencing the rates: internal and external heavy-atom effect and distortion of the planar geometry by the twisting of the phenyl rings. Comparison of the rates between PBC and $BPhCl_2$ clearly indicates the internal heavy-atom effect produced by the chlorine atoms bound to B. Since we have to consider the differences of the rates[44] it is obvious that the in-plane rates k_1 and k_2 are increased much more than the out-of-plane rate k_3 in $BPhCl_2$. This fact agrees with previous observations.[44,45]

To assess the external heavy-atom effect due to the chlorine atoms in CH_2Cl_2 we have to compare the rates of BPh_3 in CH_2Cl_2 and *n*-octane. Inspection of these rates yields a considerable increase of the in-plane rates and a small one for the out-of-plane rate. For the carbenium ions an additional external heavy-atom effect produced by the counterion $SbCl_6^-$ should be observed, since there is some evidence for an existence of ion pairs in the carbenium salts.[46,47] Indeed, for all isoelectronic pairs larger rates for the carbenium ions than for the boron compounds are found.

Comparison of the rates for PBC and BPh_3 in *n*-octane shows the effect of the distortion of the planar geometry in BPh_3. Such a distortion mixes to some extent $\sigma\pi^*$ and $\pi\sigma^*$ character into the $\pi\pi^*$ T_1 state[33] resulting in possible non-zero direct SOC matrix elements. These matrix elements lead to an enhancement of the deactivation, and indeed for the nonplanar molecule BPh_3 the rates are considerably larger than for the planar PBC. It should be mentioned also that a symmetry reduction in BPh_3 as a consequence of the phenyl ring twisting may increase the total decay rates.

Surprisingly, the comparison of BPh_3 and BPh_2Cl in CH_2Cl_2 results not in the expected increase for BPh_2Cl (due to internal heavy-atom effect), but in contrary a small decrease is observed. Two possible features can be responsible for this finding. The distortion of the planar geometry in BPh_2Cl may be smaller than in BPh_3, yielding a smaller $\sigma\pi^*$ ($\pi\sigma^*$) character in T_1 of BPh_2Cl. The other possible explanation could be the very small contribution of the chlorine atoms to the triplet wave function in BPh_2Cl. Then the external heavy-atom effect may smear out prominent differences.

Within the series of the carbenium ions many different effects influence the rates (internal heavy-atom effect by chlorine atoms, external heavy-atom effect by CH_2Cl_2 and $SbCl_6^-$, and arrangement of the phenyl rings). However, a small increase of the rates can be observed, which may be attributed to the increasing Cl substitution.

4. Experimental Section

The two salts $CPhCl_2^+/SbCl_6^-$ and $CPh_2Cl^+/SbCl_6^-$ were prepared as described in ref 48. Purified BPh_2Cl was supplied by Professor H. Nöth, Institute of Inorganic Chemistry, University of Munich.

The samples of $CPhCl_2^+/SbCl_6^-$, $CPh_2Cl^+/SbCl_6^-$, and BPh_2Cl in dried CH_2Cl_2 were degassed by three freeze-pump-thaw cycles and sealed off under vacuum into Suprasil B ampules. The concentration of all samples used here was about 10^{-3} mol/L.

Since all of the investigated molecules are very reactive with water and oxygen, the manipulations had to be done in a pure nitrogen atmosphere.

The absorption spectra of the carbenium ions were recorded at room temperature with a Perkin-Elmer (Model 330) spectrometer. The ODMR apparatus used for this work was described previously.[49,50]

5. Conclusion

The triplet states T_1 of CPh_3^+, CPh_2Cl^+, and $CPhCl_2^+$ have a completely different CT excitation behavior as compared to the T_1 states of the isoelectronic boron molecules BPh_3, BPh_2Cl, and $BPhCl_2$. The difference is already expressed in the phosphorescence spectra. Whereas the spectra of the carbenium ions consist only of broad band(s) typical for transitions with strong CT character, each of the isoelectronic boron molecules shows a vibrationally resolved spectrum which can be consistently interpreted in terms of benzenoid vibrations. Furthermore, the relatively small *D* values for the carbenium ions and the considerably larger *D* parameters for the boron molecules indicate that the T_1 wave function is strongly delocalized for the carbenium ions and, in contrast, strongly localized on the benzene ring(s) for the boron compounds. The observed difference in the CT character of the T_1 wave function between the boron and carbenium molecules is in good agreement with our calculational results, e.g., the charge densities and the amounts of intra-ring excitation (*z* values) contributing to T_1. In accordance with the experimental findings the amounts of intra-ring excitation for CPh_3^+ and CPh_2Cl^+ are zero and for $CPhCl_2^+$ are small. Here the main contributions to T_1 are CT terms. However, the amounts of intra-ring excitation for the boron molecules are considerably larger, and thus excitation in their T_1 states is mainly localized on the phenyl ring(s).

The correlation between the experiment and the calculation is also illustrated by the linear relationship between the measured *D* parameters and calculated *z* values. Experimental as well as calculational results show that the positive charge leads to a strong delocalization of the triplet electrons for the carbenium ions and thus to a strong CT character of their T_1 wave functions. On the contrary, the isoelectronic boron molecules are uncharged, and thus the T_1 wave functions are strongly localized. In spite of their different CT characters in T_1, an analogy between the carbenium and the isoelectronic boron compounds still persists. This analogy is not only expressed in the linear relationship between the *D* and *z* values but also in the similar variation of the T_1 character within both carbenium and boron series. In both series the variation is caused by the smaller electron-donating power of a chlorine when compared to a phenyl ring. Indeed, our calculations prove the contribution of the chlorine(s) to the T_1 wave function to be very small.

The total decay rates of the three ZFLs for all molecules investigated were analyzed in terms of the internal and the external heavy-atom effects and the influence of the geometry.

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