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Nature of the Contact Ion Pair CCl₃⁺Cl⁻. A Theoretical Study

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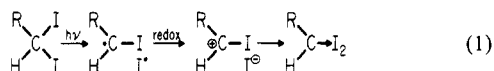Madison, Wisconsin 53706*

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We have conducted an exploratory ab initio search for a novel singlet isomer of CCl_4, corresponding to the C_{2v} "ion-pair" structure $CCl_3^+\cdots Cl^-$, as the possible source of the observed 500-nm transient feature in pulse radiolysis of liquid CCl_4. Although RHF calculations with small basis sets (STO-3G, 3-21G) give no stable minimum corresponding to this structure, a complete RHF/6-31G* calculation was found to lead to a true local C_{2v} minimum, with geometrical parameters ($R_{Cl\cdots Cl}$ = 2.63 Å, R_{C-Cl} = 1.64, 1.67 Å) and charge distribution characteristic of an ion pair. Further investigation of spin coupling and correlation effects by UHF/6-31G* and MP2/3-21G methods suggests that the ion-pair singlet is greatly stabilized (relative to other low-lying dissociation products and to the competing $Cl_2C\cdots Cl_2$ complex) by electron correlation. Estimates are offered to suggest that full MP2/6-31G* treatment would make the singlet ion-pair $CCl_3^+\cdots Cl^-$ species about 8 kcal/mol more stable than competing singlet or triplet biradical species. The longevity of such a species, relative to the "normal" covalent T_d isomer, should be further enhanced by solvation of CCl_3^+ in CCl_4 under the experimental radiolysis conditions. We therefore conclude that such charge-transfer-stabilized ion pairs (suggested also by various other lines of theoretical and experimental evidence) are plausible sources of the transient 500-nm absorbance of CCl_4 pulse radiolysis and warrant further ab initio investigation.

I. Introduction

The importance of bond–antibond ($\sigma-\sigma^*$) and lone pair–antibond ($n-\sigma^*$) interactions in stabilizing molecular conformers[1] and hydrogen-bonded complexes[2,3] has been demonstrated theoretically by Weinhold and co-workers, using the method of natural bond orbital (NBO) analysis.[2,4,5] These workers have shown that hydrogen-bonded complexes (of type $H_2O\cdots HOH$, $OC\cdots HF$, $H_3N\cdots HF$, etc.) are predominantly stabilized by $n-\sigma^*$ interactions,[6] and thus may be classified as $n-\sigma^*$ complexes. Independently, Weiss et al.[7] have found experimental support for the importance of $n-\sigma^*$ stabilization, particularly in compounds of the type $R_2C-I-I \leftrightarrow R_2C-I^+I^-$.

Such $n-\sigma^*$ complexes are also possible intermediates in the Pienta–Kropp reaction for cyclopropanation of olefins via irradiated *gem*-diiodides.[8] This process involves light-induced homolytic cleavage of one of the C–I bonds, followed by electron transfer within the resulting radical pair cage. This ion pair can rearrange to give an iodine–carbene complex, which may function as the cyclopropanation agent:

$$\begin{array}{c}\text{R}\\\text{H}\end{array}\!\!C\!\!\begin{array}{c}\text{I}\\\text{I}\end{array}\xrightarrow{h\nu}\begin{array}{c}\text{R}\\\text{H}\end{array}\!\!C\!-\!\text{I}\atop\text{I}^{\cdot}\xrightarrow{\text{redox}}\begin{array}{c}\text{R}\\\text{H}\end{array}\!\!\overset{\oplus}{C}\!-\!\text{I}\atop\text{I}^{\ominus}\longrightarrow\begin{array}{c}\text{R}\\\text{H}\end{array}\!\!C\!\!\rightarrow\!\text{I}_2 \qquad (1)$$

Weiss proposed[7] that this iodine–carbene complex is a three-center, four-electron hypervalent species with $n-\sigma^*$ stabilization and thus electronically closely related to trihalide ions X_3^-.

Analogous $n-\sigma^*$ complexes of type $R_2C-X^+X^-$ are also possible intermediates in pulse radiolysis experiments in liquid CCl_4.[9-15] In these experiments, a transient absorption is observed at around 500 nm with initial (approximately) exponential decay and a lifetime of 33 ± 3 ns (at −22 °C). Bühler and Hurni,[9] from detailed scavenger studies, initially assigned this absorption to a contact ion pair between CCl_3^+ and Cl^-, which quickly decays (with an activation energy of 2.6 ± 0.5 kcal/mol) to form CCl_4. We felt that this transient intermediate could be trichlorocarbenium chloride, $Cl_2C-Cl-Cl \leftrightarrow Cl_2C-Cl^+Cl^-$, which is planar and stabilized by $n-\sigma^*$ contact (strong interaction of Cl^- with the C–Cl antibond that it is facing). This proposed complex has C_{2v} symmetry and is depicted in Figure 1.

Bühler and co-workers[10] theoretically investigated the possibility of a stable CCl_3^+/Cl^- contact ion pair in SCF calculations with the STO-3G basis set. They only considered a nonplanar C_{3v} geometry (rather than the proposed planar C_{2v} ion pair), with Cl^- sitting above CCl_3^+ along its C_3 axis. They found no barrier for attack by Cl^- on the carbon of CCl_3^+ in this geometry. Concluding that no stable *contact* ion pair structure exists, they then modified their assignment of the 500-nm band to a solvent-separated ion pair, though an electrostatic model calculation gave a stabilization energy in liquid CCl_4 of only 0.5 kcal/mol for such a complex. Other groups have assigned the 500-nm band to CCl_4^+,[11] $CCl_4^+\cdots Cl^-$,[12,13] and "a product resulting from geminately recombining ions".[14] Bühler critically discusses these conflicting assignments, giving detailed arguments for the assignment to the CCl_3^+/Cl^- solvent-separated ion pair and against the other assignments.[15]

(1) T. K. Brunck and F. Weinhold, *J. Am. Chem. Soc.*, **101**, 1700 (1979); J. Tyrell, R. B. Weinstock, and F. Weinhold, *Int. J. Quantum Chem.*, **19**, 781 (1981); G. Wesenberg and F. Weinhold, *Int. J. Quantum Chem.*, **21**, 487 (1982).

(2) R. B. Weinstock, Ph.D. Thesis, University of Wisconsin—Madison, 1981; R. B. Weinstock and F. Weinhold, University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-661, 1981; A. E. Reed and F. Weinhold, *J. Chem. Phys.*, **78**, 4066 (1983).

(3) L. A. Curtiss, D. J. Pochatko, A. E. Reed, and F. Weinhold, *J. Chem. Phys.*, **82**, 2679 (1985); A. E. Reed, F. Weinhold, L. A. Curtiss, and D. J. Pochatko, submitted for publication.

(4) J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.*, **102**, 7211 (1980); J. E. Carpenter and F. Weinhold, submitted for publication.

(5) A. E. Reed, R. B. Weinstock, and F. Weinhold, *J. Chem. Phys.*, in press.

(6) A similar classification was suggested on empirical grounds for many van der Waals molecules by K. C. Janda, J. M. Steed, S. E. Novick, and W. Klemperer, *J. Chem. Phys.*, **67**, 5162 (1977).

(7) R. Weiss, H. Wolf, V. Schubert, and T. Clark, *J. Am. Chem. Soc.*, **103**, 6142 (1981); W. Reinhardt, Ph.D. Thesis, Universität Erlangen-Nürnberg, 1984; R. Weiss and W. Reinhardt, unpublished work.

(8) N. J. Pienta and P. J. Kropp, *J. Am. Chem. Soc.*, **100**, 655 (1978).

(9) R. E. Bühler and B. Hurni, *Helv. Chim. Acta*, **61**, 90 (1978).

(10) H.-U. Gremlich, T. K. Ha, G. Zumofen, and R. E. Bühler, *J. Phys. Chem.*, **85**, 1336 (1981).

(11) R. Cooper and J. K. Thomas, *Adv. Chem. Ser., No.* **82**, 351 (1968).

(12) R. Mehnert, J. Bös, and O. Brede, *Radiochem. Radioanal. Lett.*, **51**, 47 (1982).

(13) T. Sumiyoshi, S. Sawamura, Y. Koshikawa, and M. Katayama, *Bull. Chem. Soc. Jpn.*, **55**, 2341 (1982).

(14) C. A. M. van den Ende, L. H. Luthjens, J. M. Warman, and A. Hummel, *Radiat. Phys. Chem.*, **19**, 455 (1982).

(15) R. E. Bühler, *Radiat. Phys. Chem.*, **21**, 139 (1983).

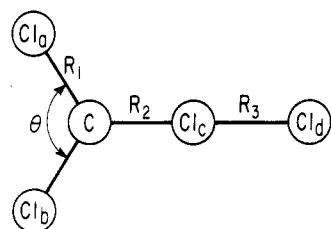**Figure 1.** Atom labeling and geometric parameters.

In view of the structural relationship of the postulated Cl_2C–Cl–Cl species to the R_2C–I–I compounds and to the interpretation of these pulse radiolysis experiments, we undertook an ab initio study of the stability and geometry of this species and an NBO analysis of its bonding. Although a definitive numerical treatment of this 74-electron species (with large basis sets, full effects of electron correlation, complete geometry optimization of the ion pair and other low-lying isomers or dissociation products, etc.) would be quite prohibitive, we have nevertheless been able to verify that such a complex *does exist* at a fairly realistic level of ab initio theory and to approximately characterize its structure and energetics. The proposed C_{2v} ion-pair isomer lies high in energy above the T_d covalent (global minimum) isomer but seems to be shielded by activation barriers from rearrangements to other isomeric forms.

An important side issue, related to the previous work of Bühler and co-workers,[10] is to consider the possible effects of solvation on the CCl_3^+/Cl^- recombination reaction as it would occur in the liquid CCl_4 pulse radiolysis experiments. It is conceivable that the C_{3v} path of attack studied by Bühler is blocked by complexation of the low-occupancy carbon p orbital of CCl_3^+ with a molecule of CCl_4 on either side. Such complexation would effectively force an in-plane C_{2v} attack of Cl^- on CCl_3^+, leading initially to the formation of the proposed Cl_2C–Cl^+Cl^- (solvated) complex, regardless of the existence or absence of a barrier for the gas-phase C_{3v} attack. In this study we therefore also carried out a preliminary investigation of solvation effects, by studying various solvated complexes $CCl_3^+(CCl_4)_n$ ($n = 1$, 2) by the semiempirical INDO–SCF–MO method. Taken together with previous mechanistic investigations of diiodocarbenes, the results of this paper suggest that a novel class of contact-ion-pair "n–σ^* complexes" may play an important role in the chemistry of heavier halides and halocarbenium ions.

II. Ab Initio Calculations

In this section we report the results of an ab initio search for a minimum in the restricted Hartree–Fock (RHF) potential surface for the proposed trichlorocarbenium chloride species of C_{2v} symmetry. Such a minimum could only be found when a sufficiently flexible basis set was employed, including d functions. We then discuss how the results of the RHF calculations might be altered by inclusion of electron correlation. The general features of the RHF ion-pair wave function, particularly the role of n–σ^* charge transfer, are discussed by means of natural bond orbital (NBO) analysis.

A. Methods. Ab initio SCF studies with the "sp" basis sets STO-3G[16] and 3-21G[17] were carried out using the GAUSSIAN 80 program system,[18] and additional studies with the "spd" basis sets 6-31G*[19] and 6-31+G*[20] were carried out with the GAUSSIAN 82

(16) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **52**, 2769 (1970).

(17) J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 939 (1980); M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, *J. Am. Chem. Soc.*, **104**, 2797 (1982).

(18) P. N. van Kampen, F. A. A. M. de Leeuw, C. F. Smits, and C. Altona, "Gaussian 80", QCPE Program No. 437, Indiana University, Bloomington, IN, 1981. This is an IBM modification of the original GAUSSIAN 80 program: J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, *QCPE*, **13**, 406 (1981).

(19) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972); P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).

	total energy, au		ΔE (Cl + e⁻ → Cl⁻), kcal/mol
basis set	Cl (UHF)	Cl⁻ (RHF)	
STO-3G	−454.542 192	−454.480 422	+38.8
3-21G	−457.276 551	−457.353 585	−48.3
6-31G	−459.442 939	−459.524 551	−51.2
6-31+G	−459.443 759	−459.538 279	−59.3
6-31G*	−459.447 964	−459.525 997	−49.0
6-31+G*	−459.448 712	−459.539 661	−57.1
STO[b]	−459.481 87	−459.576 70	−59.5
expt			−83.3

[a] The electron affinity (EA) is the negative of these quantities. [b] Minimal basis of Slater type orbitals, individually optimized for Cl and Cl⁻; see ref 27.

TABLE II: Cl₂ and CCl₃⁺ Optimized Geometries and Energies (RHF Level)

	Cl₂		CCl₃⁺	
basis set	R, Å	energy, au	R, Å	energy, au
STO-3G	2.063	−909.115 117	1.721	−1400.771 948
3-21G	2.193	−914.543 934[a]	1.703	−1409.110 756
6-31G	2.157	−918.872 968		
6-31+G	2.154	−918.875 783		
6-31G*	1.990	−918.912 817	1.643	−1415.945 760
6-31+G*	1.990[b]	−918.914 683		

[a] MP2/3-21G energy is −914.646 376 au. [b] Nonoptimized parameter.
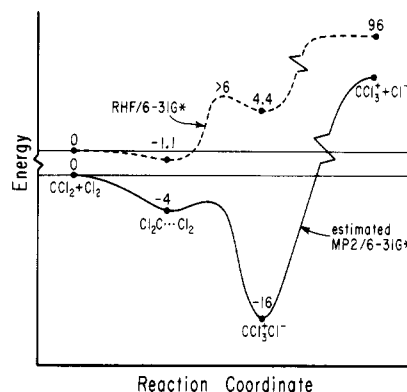
Figure 2. Hypothetical potential energy curves depicting the Cl_2C⋯Cl_2 and CCl_3^+⋯Cl^- complexes and their respective dissociation limits, based on the calculations of this work. The dashed curve is based on RHF/6-31G* results (geometry optimized), and the solid curve includes correlation corrections estimated from MP2/3-21G calculations (see text). All numbers are given in kcal/mol relative to the $CCl_2 + Cl_2$ dissociation limit (at the respective level of approximation) and are for illustrative purpose only. In particular, the positions and heights of the intermediate barriers are not accurately known for either curve. (See also text, sections II.C. and II.D.)

program system.[21] The resulting wave functions were analyzed by the natural bond orbital procedure.[4,5,22] The effects of valence electron correlation were studied by second-order Møller–Plesset perturbation theory (MP2)[23] with the GAUSSIAN 82 system, employing the frozen core approximation. RHF geometry optimizations with the STO-3G and 3-21G basis sets employed the gradient method.[24] The RHF/6-31G* geometry optimizations

(20) T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. v. R. Schleyer, *J. Comput. Chem.*, **4**, 294 (1983). See also M. J. Frisch, J. A. Pople, and J. S. Binkley, *J. Chem. Phys.*, **80**, 3265 (1984).

(21) J. S. Binkley, M. J. Frisch, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, E. M. Fluder, and J. A. Pople, "Gaussian 82" (release A version), Carnegie-Mellon University, Pittsburg, PA, 1983.

(22) The NBO program as described in ref 4 and 5 was implemented by one of the authors (A.E.R.) into link 601 of the GAUSSIAN 82 system.

(23) J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem.*, *Symp.*, No. **10**, 1 (1976).

TABLE III: CCl$_2$ Optimized Geometries and Energies

basis set	singlet (RHF)			triplet (UHF)		
	R, Å	θ, deg	energy, au	R, Å	θ, deg	energy, au
STO-3G	1.803	106.86	−946.431 756	1.760	124.48	−946.450 369
3-21G	1.848	107.13	−952.103 805^a	1.784	124.26	−952.117 096
6-31G	1.810	109.45	−956.634 453	1.757	126.49	−956.652 425
6-31+G	1.808	109.54	−956.638 615			
6-31G*	1.711	110.30	−956.712 261	1.687^c	126.95^c	−956.723 637^c
6-31+G*	1.711^b	110.30^b	−956.715 804			

^{a}MP2/3-21G energy is −952.283 412 au. ^{b}Nonoptimized parameters. ^{c}Reference 29.

TABLE IV: Results of Singlet C$_{2v}$ RHF Geometry Optimizations of CCl$_4$^{a}

basis set	structure	constraint	species	R_1	R_2	R_3	θ	rel energy
STO-3G	1	$R_2 = \infty$	Cl$_2$C, Cl$_2$	1.803	∞	2.063	106.86	0.00
STO-3G	2	none	Cl$_2$C⋯Cl$_2$	1.802	3.486	2.063	106.90	−0.17
STO-3G	3	$R_3 = \infty$	Cl$_2$CCl$^+$, Cl$^-$	1.721	1.721	∞	120.00	184.8
3-21G	4	$R_2 = \infty$	Cl$_2$C, Cl$_2$	1.848	∞	2.193	107.13	0.00 (0.00)^b
3-21G	5	none	Cl$_2$C⋯Cl$_2$	1.831	2.843	2.208	108.10	−1.93 (−4.80)^b
3-21G	6	$R_1 = R_2$	Cl$_2$CCl$^+$⋯Cl$^-$	1.767	1.767	2.536	115.34	16.4 (−4.09)^b
3-21G	7	$R_3 = \infty$	Cl$_2$CCl$^+$, Cl$^-$	1.703	1.703	∞	120.00	115.1
6-31G*	8	$R_2 = \infty$	Cl$_2$C, Cl$_2$	1.711	∞	1.990	110.30	0.00
6-31G*	9	none^c	Cl$_2$C⋯Cl$_2$	1.700	2.840	2.000	111.00	−1.06
6-31G*	10	none	Cl$_2$CCl$^+$⋯Cl$^-$	1.666	1.639	2.634	117.40	4.39
6-31G*	11	$R_3 = \infty$	Cl$_2$CCl$^+$, Cl$^-$	1.643	1.643	∞	120.00	96.2

^{a}See Figure 1 for definitions of geometrical parameters; all bond lengths in Å, angles in deg, and relative energies in kcal/mol. ^{b}Relative MP2/3-21G energies. ^{c}Structure not opttimized, but chosen by analogy to **5** (see text, ref 25).

were carried out by parabolic fits to single-point calculations. The charge-transfer energy was evaluated by the NBO method,[2,3] by zeroing elements of the NBO Fock matrix that connect the high-occupancy NBOs (cores, lone pairs, and bonds) of one monomer with the low-occupancy NBOs (antibonds and Rydbergs) of the other, and by computing the energy change that results.

B. RHF Geometry Optimizations. Singlet RHF geometry optimizations were performed on the planar CCl$_4$ complex shown in Figure 1, which was restricted to C_{2v} symmetry and has four geometrical parameters. This complex has two extreme limits: $R_2 = \infty$ (separated CCl$_2$ and Cl$_2$) and $R_3 = \infty$ (separated CCl$_3$$^+$ and Cl$^-$ or CCl$_3$ and Cl). Optimized geometries and energies of Cl, Cl$^-$, CCl$_3$$^+$, Cl$_2$, and CCl$_2$ are given in Tables I–III. There are two possible energy minima between these two limits. The first, with long R_2, corresponds to the weakly bound complex Cl$_2$C⋯Cl$_2$. The other, with much shorter R_2, corresponds (with an RHF singlet wave function) to the proposed strongly interacting ion pair CCl$_3$$^+$⋯Cl$^-$, trichlorocarbenium chloride. Both of these minima were investigated with the STO-3G, 3-21G, and 6-31G* basis sets, with the results shown in Table IV and Figure 2.

The Cl$_2$C⋯Cl$_2$ structures will be discussed first. The intermolecular distance R_2 for this complex decreases from 3.486 to 2.843 Å on improvement from the STO-3G to the 3-21G basis. This dramatic change is probably due to the poor electron affinity of the chlorine atom with the STO-3G basis (of the wrong sign; see Table I), which effectively prevents the small buildup of negative charge at the terminal chlorine (Cl$_d$) that occurs in the complex with the 3-21G basis. At the 3-21G level, small intramolecular geometry changes occur: the bond of Cl$_2$ stretches by 0.015 Å, the carbene C–Cl bond contracts by 0.017 Å, and the carbene bond angle expands by 0.97°. As can be seen from Table IV, these intermolecular changes on going from separated CCl$_2$ and Cl$_2$ (structure **4**) to interacting CCl$_2$ and Cl$_2$ (**5**) are all in the direction of the separated CCl$_3$$^+$ and Cl$^-$ limit (**7**).

Since the structure of the Cl$_2$C⋯Cl$_2$ complex cannot be expected to qualitatively change upon improvement to the 6-31G* basis set level, and our main focus was on the search for the ion-pair structure, an optimization of the Cl$_2$C⋯Cl$_2$ structure was not done at this level. Instead, the 6-31G* optimum geometries for CCl$_2$ and Cl$_2$ (**8**) were adjusted by small amounts and the 3-21G value

of the intermolecular distance R_2 was used.[25] As expected, the binding energy of the complex decreased, from 1.93 kcal/mol (3-21G basis, **5**) to 1.06 kcal/mol (6-31G* basis, **9**). The 6-31G* binding energy would increase upon geometry optimization, but probably not by more than several tenths of a kcal/mol.

More extensive effort was aimed at finding the proposed second energy minimum that has a much shorter value of R_2 or proving that it does not exist. Despite thorough and exhaustive searches, no such minimum could be located with the STO-3G and 3-21G basis sets.[26] It is not expected that a larger sp basis set, such as 6-31G, would result in any qualitative change from the 3-21G result. However, Tables II and III indicate that the addition of d functions to the basis set (going from 6-31G to 6-31G*) changes the geometries of Cl$_2$, CCl$_3$$^+$, and CCl$_2$ significantly. It may be supposed that addition of d functions gives the central chlorine atom (Cl$_c$) of the complex an orbital flexibility that can be used to overcome some of the severe steric repulsion between Cl$_c$ and Cl$_d$ that will occur in the ion-pair structure, particularly through the d$_{z^2}$ function (which lies along the C_{2v} axis).

Therefore, a 6-31G* RHF geometry search was done, and a true minimum in the C_{2v} potential energy surface (structure **10** in Table IV) was obtained. (We did not test for the breaking of the C_{2v} symmetry because we found that **5** and **6** at the RHF/3-21G level are stable with respect to out-of-plane bending about Cl$_c$ and about C.) From a starting structure ($R_1 = 1.66$ Å, $R_2 = 1.70$ Å, $R_3 = 2.04$ Å, $\theta = 115.0°$) with an energy 33.3 kcal/mol above that for separated CCl$_2$ and Cl$_2$, R_3 was stretched to 2.34 Å (by analogy with **6**) and the relative energy dropped to +9.8 kcal/mol. Stretching of R_2 to 1.80 Å then increased the relative energy to +10.9 kcal/mol, showing a resistance toward approach of the Cl$_2$C⋯Cl$_2$ minimum. Initial optimization of R_3 with all other parameters fixed (R_2 being set to 1.70 Å) increased R_3 to 2.64 Å and lowered the relative energy still further to 5.71

(24) H. B. Schlegel, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **80**, 1976 (1984), and references therein.

(25) As the 3-21G basis usually overestimates intermolecular interaction energies compared to the 6-31G* basis (due to greater superposition error), the monomer geometries were adjusted by somewhat smaller amounts than would be suggested by the 3-21G results above. The bond length of Cl$_2$ (R_3) was lengthened by 0.010 Å, the carbene C–Cl bond length (R_1) was shortened by 0.011 Å, and the carbene bond angle (θ) was expanded by 0.70°.

(26) A 3-21G minimum could be found by setting the artificial constraint $R_2 = R_1$, which forces all three C–Cl bonds to be of the same length, and then optimizing the three parameters R_1, R_3, and θ. This results in **6** (see Table IV), which is 18 kcal/mol above the Cl$_2$C⋯Cl$_2$ minimum for this basis set (**5**). When the $R_2 = R_1$ constraint is released, gradient optimization leads back to **5**, due to the large and opposite forces on the C–Cl bonds that exist in **6**.

kcal/mol. Full optimization then reduced the relative energy to +4.39 kcal/mol and proved that a second minimum does exist at the RHF/6-31G* level of theory, as indicated in Figure 2. The geometry search was carried out to the point of optimizing the total energy of the structure to within 10^{-5} au, yielding an energy of -1875.61808 au and a geometry of $R_1 = 1.666$ Å, $R_2 = 1.639$ Å, $R_3 = 2.634$ Å, $\theta = 121.3°$.

Comparison of **10** and **11** in Table IV shows that the ion-pair structure closely resembles the separated CCl$_3^+$/Cl$^-$ limit. In the ion pair, the angle θ has closed by 2.6°, the end C–Cl bonds have lengthened by 0.023 Å, and the central C–Cl bond has contracted by 0.004 Å. The stabilization of the ion pair relative to the separated ions is 92 kcal/mol. Since, as it is nearly a chloride ion, the end chlorine atom (Cl$_d$) has a high negative charge, it is important that the basis set be sufficiently flexible to describe a chloride ion as well as a chlorine atom.

Anions are more difficult to describe than atoms because they require extra orbitals of diffuse extent. A further problem is that atomic basis sets are normally optimized for atoms in a covalent (rather than anionic) environment. Thus, there are serious reasons for questioning whether the 6-31G* basis set has a bias against the buildup of negative charge on Cl$_d$. If this bias exists, the stability of the ion pair will be underestimated. One criterion for examining this basis set balance between Cl and Cl$^-$ is the electron affinity of the chlorine atom, which is listed in Table I for various basis sets. Addition to the 6-31G* basis of a diffuse uncontracted sp shell to each atom, forming what is denoted as the 6-31+G* basis, leads to an improvement of the electron affinity by 8.1 kcal/mol to 57.1 kcal/mol. Although still far from experiment (presumably due in part to correlation effects), this value is close to the 59.5 kcal/mol value obtained[27] with a minimal basis of STO orbitals optimized individually for Cl and Cl$^-$. To test the effect of the extra diffuse functions, a calculation on **10** with the 6-31+G* basis was done, yielding an energy of +3.70 kcal/mol relative to separated CCl$_2$ and Cl$_2$ in the same basis at their 6-31G* geometries. That the relative energy of **10** is decreased by only 0.69 kcal/mol (rather than by around 8 kcal/mol) suggests that the chloride ion bound in the ion pair is significantly less diffuse than is an isolated chloride ion.

C. UHF Calculations. As is well-known, the closed-shell RHF method gives the wrong (ionic) dissociation limit for closed-shell diatomic molecules, whereas the UHF method (which allows molecular orbitals of different spin to vary independently) gives the correct atomic dissociation limit. This leads one to question the validity of the RHF wave function found for the CCl$_3^+$/Cl$^-$ ion pair, since, as R_3 is stretched, an ionic limit is approached. Indeed, if one transfers an electron from Cl$^-$ to CCl$_3^+$ in **11**, one finds that, at the UHF/6-31G* level, the limit of the separated radicals, CCl$_3$ and Cl, is 133.5 kcal/mol lower in energy than the limit of the separated ions CCl$_3^+$ and Cl$^-$. This unrelaxed CCl$_3$/Cl limit is 42.7 kcal/mol more stable than the structure **10** ion pair. The magnitudes of these numbers would increase upon optimization of the geometry of CCl$_3$. Thus, the question of the validity of the RHF wave function for **10** must be examined.

To investigate this question, an electron was transferred from the HOMO (of π symmetry, mainly localized on Cl$_d$) to the LUMO (also of π symmetry, mainly localized on the CCl$_3^+$ fragment) of the RHF/6-31G* wave function for **10**, and a singlet UHF wave function was optimized. The energy decreased by 30.39 kcal/mol from the RHF value, but the value of S^2 (1.11) indicated that the "singlet" wave function was severely contaminated with triplet character, and this wave function was not considered further. A similar procedure was employed in optimizing a triplet UHF wave function, resulting in a more satisfactory wave function (with $S^2 = 2.025$) that has an energy 29.61 kcal/mol below the RHF result.

Caution must be exercised, however, in comparing the energy of a singlet with that of a triplet, especially at the SCF level. From its reactivity pattern in carbene insertion reactions, it is known experimentally that the ground state of CCl$_2$ is a singlet. (This

(27) L. Gianolio and E. Clementi, *Gazz. Chim. Ital.,* **110**, 179 (1980).

TABLE V: CCl$_2$ Singlet–Triplet Separation (Δ_{S-T})

method/basis set[a]	Δ_{S-T}, kcal/mol[b]
HF/STO-3G	11.68
HF/3-21G	8.34
HF/6-31G	11.28
HF/6-31G*[c]	7.14
MP2/6-31G*[c]	−13.29
MP3/6-31G*[c]	−12.59
MP4DQ/6-31G*[c]	−12.97
MP4SDQ/6-31G*[c]	−14.14
MCSCF/DZ[d]	−2.9
MCSCF/DZ + d on C[d]	−13.5

[a] All calculations are at the optimal singlet RHF and triplet UHF geometries for the particular basis set. [b] $\Delta_{S-T} = E(\text{singlet}) - E(\text{triplet})$. [c] Reference 29. [d] Two-term MCSCF for singlet and one-term SCF for triplet, using double-ζ basis set with and without an optimized d function on carbon (from ref 30).

is due to π stabilization by the chlorine lone pairs of the empty carbon p orbital and is in contrast to the triplet ground state of CH$_2$). Table V shows however that the HF/6-31G* singlet–triplet separation is of the wrong sign and that electron correlation (which will be larger in the singlet than in the triplet state) must be considered in order to get a meaningful comparison of these states.

D. Effects of Electron Correlation. There are strong reasons to suppose that correlation will significantly favor the CCl$_3^+$/Cl$^-$ ion pair with respect to the weakly bound CCl$_2$/Cl$_2$ complex. Since it is a cation, CCl$_3^+$ has many low-lying virtual MOs, and since Cl$^-$ is an anion, it has several high-lying occupied MOs, leading to small HOMO–LUMO gaps for CCl$_3^+$/Cl$^-$. This is borne out by the orbital energies and HOMO–LUMO gaps listed in Table VI. For example, the π HOMO–LUMO gap (B$_1$ symmetry) in CCl$_3^+$/Cl$^-$ is less than half of what it is in CCl$_2$/Cl$_2$, which will lead to larger electron correlation effects.

To investigate these effects more quantitatively, electron correlation was included by using the MP2 method with the 3-21G basis set. MP2/3-21G calculations were done at the RHF/3-21G geometries of separated CCl$_2$ and Cl$_2$ (**4**), CCl$_2$/Cl$_2$ (**5**), and CCl$_3^+$/Cl$^-$ (**6**), yielding total energies of $-1866.929\,788$, $-1866.937\,423$, and $-1866.936\,299$ au, respectively (the relative energies are given in Table IV). At the RHF/3-21G level, the CCl$_3^+$/Cl$^-$ structure is 18.3 kcal/mol in energy above the CCl$_2$/Cl$_2$ structure, and there is only a single potential energy minimum, the CCl$_2$/Cl$_2$ structure. With MP2, the CCl$_3^+$/Cl$^-$ structure is only 0.71 kcal/mol above the CCl$_2$/Cl$_2$ structure and 4.09 kcal/mol *more* stable than separated CCl$_2$ and Cl$_2$. Thus, with the 3-21G basis set, correlation stabilizes CCl$_3^+$/Cl$^-$ by 17.6 kcal/mol with respect to CCl$_2$/Cl$_2$, a dramatic effect. Though we have not carried out an MP2/3-21G geometry search, it is quite likely that there are two minima, corresponding to CCl$_3^+$/Cl$^-$ and to CCl$_2$/Cl$_2$, with a barrier between these two structures. The 10% greater correlation energy found with MP2 for the CCl$_3^+$/Cl$^-$ structure than for CCl$_2$/Cl$_2$ thus appears to create an energy minimum that did not exist at the HF level with the 3-21G basis set.

Since the HOMO–LUMO gaps within the different symmetry groups for the two interacting structures (**5** and **6**) at the RHF/3-21G level are rather similar to those mentioned at the RHF/6-31G* level, it is reasonable to suppose that the correlation effect on the relative energies should be at least as strong with MP2/6-31G* as with MP2/3-21G. Although such calculations were not carried out directly, one could therefore estimate from Table IV that, at the MP2/6-31G* level, CCl$_3^+$/Cl$^-$ will be about 12 kcal/mol *more* stable than CCl$_2$/Cl$_2$. More extensive calculations employing even larger basis sets and/or methods that can recover a larger fraction of the correlation energy would likely tend to favor CCl$_3^+$/Cl$^-$ over CCl$_2$/Cl$_2$ even more strongly.[28] The

(28) These assertions are supported by the data in Table VI, which show that the HOMO–LUMO gaps for the structure **10** "neutral atom" triplet are, with one minor exception, larger than for the structure **9** "neutral atom" singlet and, without exception, much larger than for the structure **10** "ion-pair" RHF singlet.

TABLE VI: Orbital Energies and Energy Gaps (in au)

	MO symmetry[a]	HOMO[b]	LUMO[b]	HOMO → LUMO gaps[b]
CCl₄, **10**, RHF/	A₁	−0.313	+0.060, +0.192	0.373, 0.505
6-31* singlet	B₁	−0.309	−0.083	0.216
	B₂	−0.312	+0.128	0.440
CCl₄, **9**, RHF/	A₁	−0.406	+0.060	0.466
6-31G* singlet	B₁	−0.431	+0.027	0.458
	B₂	−0.431	+0.222	0.653
CCl₄, **10**, UHF/	A₁, α	−0.478	+0.141	0.619
6-31G* triplet	A₁, β	−0.461	+0.181	0.642
	B₁, α	−0.339	>0.26	>0.65
	B₁, β	−0.480	−0.048	0.432
	B₂, α	−0.456	+0.228	0.684
	B₂, β	−0.453	+0.224	0.697
	A₁	−0.323	+0.023, +0.046	0.346, 0.369
CCl₄, **10**, RHF/	B₁	−0.317	−0.087, +0.079	0.230, 0.396
6-31+G* singlet	B₂	−0.320	+0.047	0.367
	A₁	−0.399	+0.161	0.560
CCl₂, **8**, RHF/	B₁	−0.558	+0.038	0.596
6-31G* singlet[c]	B₂	−0.474	+0.229	0.703

[a] The A₂ HOMO–LUMO gaps are very high and are not listed. [b] Within each symmetry type. [c] HOMO–LUMO gaps in Cl₂ are greater than 1 au.

TABLE VII: Natural Atomic Charges in Structures 10 (Ion Pair) and 11 (Separated Ions)[a]

structure	wave function	Cl_a	C	Cl_c	Cl_d
11	RHF/6-31G*	+0.334 (+0.390)	−0.003 (−0.170)	+0.334 (+0.390)	−1.000 (−1.000)
10	RHF/6-31G*	+0.222 (+0.280)	−0.025 (−0.229)	+0.417 (+0.460)	−0.837 (−0.772)
10	RHF/6-31+G*	+0.227 (+0.312)	−0.032 (−0.548)	+0.429 (+0.688)	−0.851 (−0.764)

[a] For atom labeling and definition of structures, see Figure 1 and Table IV. Numbers in parentheses are the corresponding Mulliken charges, shown for comparison purposes only.

TABLE VIII: NBO Analysis of C–Cl Bonds in CCl₃⁺ (Structure 11) and CCl₃⁺/Cl⁻ (Structure 10)

	CCl₃⁺ RHF/6-31G*	CCl₃⁺/Cl⁻ ion pair			
		Cl_a–C bond		C–Cl_c bond	
		RHF/6-31G*	RHF/6-31+G*	RHF/6-31G*	RHF/6-31+G*
% polarization toward carbon[a]	52.4	50.5	50.7	55.1	55.2
carbon hybrid					
spd character	sp²·⁰⁰d⁰·⁰¹	sp²·¹⁹d⁰·⁰¹	sp²·²⁰d⁰·⁰²	sp¹·⁶⁸d⁰·⁰¹	sp¹·⁶⁷d⁰·⁰¹
% s character	33.24	31.25	31.09	37.24	37.27
chlorine hybrid					
spd character	sp⁴·⁵⁰d⁰·⁰⁶	sp⁴·⁴⁰d⁰·⁰⁶	sp⁴·⁶⁷d⁰·⁰⁸	sp⁶·¹⁵d⁰·¹⁰	sp⁶·⁸⁷d⁰·¹⁵
% s character	17.97	18.31	17.39	13.79	12.46

[a] A nonpolar bond would have a value of 50%.

presumed MP2/6-31G* energy curve (with the MP2 correlation contribution taken from the MP2/3-21G result) is sketched as the solid line in Figure 2. The dramatic difference between the form of this curve and that of the RHF/6-31G* curve is intended to qualitatively depict the strong effect of correlation in stabilizing the ion-pair structure.

Turning back to the question of singlet–triplet separations, one can see from Table V that MP2 changes the singlet–triplet separation of CCl₂ with the 6-31G* basis by 20.4 kcal/mol, favoring the singlet.[29] With regard to the accuracy of calculated singlet–triplet separations for carbenes, it should be noted that a value close to experiment for CH₂ can be obtained with a simple two-configuration MCSCF description of the singlet and a single configuration SCF description of the triplet.[30] This method, as shown in Table V, gives a result close to the MP2/6-31G* result for CCl₂. As shown, extension of the MP treatment to third and fourth order (excluding triple excitations) does not significantly affect the singlet–triplet separation.[29]

To make a very rough prediction of the relative energies of the singlet (CCl₃⁺/Cl⁻) and triplet biradical (CCl₃·/Cl·) states for **10**, the assumptions are made that the correlation effects favoring the singlet over the triplet and favoring an ion pair over a neutral atom species are additive and are respectively the 20 and 18 kcal/mol values found above in different contexts. Since the triplet is favored over the singlet by 30 kcal/mol at the HF/6-31G* level, the estimated total correlation effect of 38 kcal/mol leads to the prediction that the singlet is 8 kcal/mol more stable than the triplet at the MP2/6-31G* level. This is quite crude but serves to indicate that the correlation effects are quite large[31] and act to greatly stabilize the singlet ion-pair structure.

Returning to the question of the reasonableness of the RHF closed-shell approximation for **10**, one could argue that the singlet diradical should be similar in energy to the triplet diradical, since the two unpaired electrons are essentially localized on different fragments (CCl₃· and Cl·). Since, from the above arguments, there is reason to suppose that the singlet ion pair is more stable than the triplet biradical, the singlet ion pair should also be more stable

(29) R. A. Whiteside, M. J. Frisch, D. J. DeFrees, K. Raghavachari, J. S. Binkley, H. B. Schlegel, and J. A. Pople, Carnegie-Mellon University Quantum Chemistry Archive, Pittsburgh, PA 15213.

(30) C. W. Bauschlicher, H. F. Schaefer, and P. S. Bagus, *J. Am. Chem. Soc.*, **99**, 7106 (1977).

(31) As partial support for this assertion, we note from Table VI that, at the RHF/6-31+G* level for **10**, there are *five* HOMO–LUMO gaps that are less than 0.4 au in energy, whereas there are only two at the RHF/6-31G level. This indicates the importance of the diffuse functions for describing the low-energy virtual MO space.

than the singlet biradical. Although this conjecture remains to be thoroughly tested, it lends credibility to the presumption that the closed-shell RHF approximation for **10** yields a qualitatively correct wave function and, thus, that the second minimum in the RHF/6-31G* potential energy surface is not an artifact.[32]

E. NBO Analysis. Natural bond orbital (NBO) analysis,[4] and the associated natural population analysis (NPA),[5] provides a means of comparing wave functions of different species, geometry, or basis set and leads to a description of the electronic charge distribution that seems to avoid the major artifacts of the familiar Mulliken population analysis (MPA). For the RHF wave functions of **10** and **11**, we list in Table VII the calculated atomic charges, and in Table VIII, the polarizations and hybridizations of the C–Cl bonds. We first consider the analysis of the CCl_3^+ wave function (**11**) and then discuss the changes that occur upon formation of the ion pair (**10**).

For CCl_3^+, the natural charges show that the carbon atom is approximately neutral, the positive charge being borne by the chlorine atoms even though in the Lewis structure the carbon atom has a formal positive charge. (In singlet CCl_2, the natural charge on carbon is also nearly neutral, at –0.002.) The formally empty carbon π orbital gains an occupancy of 0.74e by donation from the chlorine π lone pairs, this being the major mechanism for transmitting the positive charge to the chlorine atoms.

Upon formation of the ion pair (**10**), a charge transfer of 0.16e from Cl^- to CCl_3^+ occurs, the carbon atom gaining 0.02e, Cl_a and Cl_b each gaining 0.11e, and Cl_c losing 0.08e. The changes in the σ (π) populations are found to be +0.054e (+0.058e) at Cl_a and Cl_b, +0.019e (+0.003e) at C, +0.000e (–0.083e) at Cl_c, and –0.127e (–0.036e) at Cl_d. Thus, the σ population at Cl_c is unchanged, while a significant transfer of π charge from Cl_c to Cl_a and Cl_b occurs. On improvement to the 6-31+G* basis, the natural atomic charges are nearly unchanged, the largest change being only 0.014e. For comparison, the Mulliken charges are also presented in Table VII. In contrast to natural charges, these seem to change dramatically upon the addition of the diffuse (+) functions, with carbon changing by 0.31e to end up with a rather large negative charge (–0.55). This is in line with other experience indicating the unsatisfactory character of Mulliken populations for diffuse basis functions and the greater usefulness of the NPA procedure for comparing wave functions in different basis sets.[5]

In accord with the aforementioned changes in atomic charges upon ion-pair formation, the C–Cl_a bond becomes more polarized toward chlorine and the C–Cl_c bond becomes more polarized toward carbon, so that Cl_c is effectively more electropositive than the other two chlorine atoms bonded to carbon. The hybridization changes in the ion pair are all consistent with Bent's rule,[33] which suggests that the s character of an atom will concentrate in the hybrids directed toward the most electropositive substituents. Thus, in Table VIII we can see that the carbon hybrid directed toward Cl_c is $sp^{1.68}d^{0.01}$, with 6% greater s character than the other two carbon hybrids. The chlorine hybrids show similar correlations with the bond polarizations in their s character. The C–Cl bonding NBOs do not significantly change upon addition of the diffuse (+) functions.

A major reason for the increased positive charge on Cl_c in the ion pair is the strong repulsion between Cl_c and Cl_d due to the Pauli exclusion principle. This increased positive charge also enhances the n–σ^* charge-transfer energy: As the C–Cl_c bond becomes more polarized toward carbon, the C–Cl_c antibond becomes more polarized toward Cl_c, increasing its interaction with the chloride lone pairs. The total charge-transfer stabilization energy estimated by the NBO deletion method[2,3] is quite significant, 32 and 30 kcal/mol for RHF/6-31G* and RHF/6-

31+G*, respectively.[34] The relative importance of the various possible charge-transfer interactions between individual orbitals can be estimated by zeroing individual elements of the NBO Fock matrix and recomputing the energy.[2,3] In this manner, about 80% of the computed charge-transfer stabilization can be identified with the n–σ^* interaction from chloride into $\sigma^*_{C-Cl_c}$, the remainder being associated with charge transfer into various Rydberg orbitals on Cl_c. The strong charge-transfer interaction will help the complex to overcome some of the chlorine–chlorine repulsion, and without it, the Cl–Cl distance would be significantly longer (the Cl–Cl distance, 2.63 Å, is about 1 Å shorter than the Cl–Cl van der Waals contact distance).

NBO analysis of the UHF/6-31G* triplet wave function for **10** (the triplet biradical) led to results that were similar to those for the isolated radicals CCl_3 and Cl. The analyses of the UHF/6-31G* singlet and triplet wave functions for **10** are nearly identical (differing at most in the third significant figure in their natural populations, hybridizations, and bond polarizations, with the α and β spin populations on Cl_d being reversed), which further emphasizes the very strong triplet contamination in the $S^2 = 1.11$ "singlet" wave function.

III. Semiempirical Calculations

A. Cl_2C–Cl–Cl Complex. Preliminary semiempirical studies on the C_{2v} ion-pair species were carried out using the INDO method[35] with Gordon's parametrization for second-row atoms,[36] using the BONDO program system.[37] Associated calculations with the MNDO method (not reported here) were also carried out on this species, leading to similar results. The optimum INDO geometry is $R_1 = 1.64$ Å, $R_2 = 1.72$ Å, $R_3 = 1.99$ Å, $\theta = 113.0°$. The INDO binding energy is 64.8 kcal/mol relative to separated CCl_2 (singlet) and Cl_2 and 171.8 kcal/mol relative to separated CCl_3^+ and Cl^-. Due to the depth of this minimum, no minimum corresponding to weakly interacting CCl_2 and Cl_2 was found to exist.

What is the origin of the very large discrepancy between the ab initio and semiempirical values of the Cl–Cl (R_3) distance in trichlorocarbenium chloride? It should be recognized that, in addition to their other limitations and defects, these semiempirical methods give the wrong sign for the electron affinity of chlorine (as does the ab initio STO-3G method). Thus, the INDO chlorine electron affinity is –22 kcal/mol. This makes Cl^- an unrealistically powerful electron donor, resulting in electron transfers from Cl^- to CCl_3^+ in the optimized INDO (MNDO) "ion-pair" structure of 0.63 (0.57) electron, compared to the RHF/6-31G* value of only 0.16e. The result of this strong charge transfer is the short Cl–Cl distance.[38]

Despite these limitations, semiempirical methods can provide useful information concerning some of the general trends in these complexes. Weiss and Macheleid[39] have shown that MNDO is useful in studying trends in the properties of various substituted halocarbenium halides.

B. Complexation of CCl_3^+ with CCl_4. To investigate the possible effects of solvation of CCl_3^+ by CCl_4, we first optimized

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(32) There is independent experimental evidence suggesting the stability of the ion pair over the biradical, based on the mechanistic studies of Pienta and Kropp (ref 8) on the reactivity of irradiated *gem*-diiodes. They found, as is depicted in eq 1, that the biradical initially produced by the absorption of radiation has a strong tendency to undergo electron transfer to form the corresponding ion pair. Thus, at least for an iodo species, the ion pair is apparently more stable than the biradical.

(33) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(34) These estimates of the charge-transfer energy do not take into account internal rehybridization or repolarization energy. It must be stressed that these numbers are estimates and may neglect important higher order effects, since the charge-transfer process induces in this case a much stronger perturbation on the electronic structure than is the case in the previously studied hydrogen-bonded molecular complexes.

(35) J. A. Pople and D. A. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970.

(36) M. S. Gordon, M. D. Bjorke, F. J. Marsh, and M. S. Korth, *J. Am. Chem. Soc.*, **100**, 2670 (1978).

(37) F. Weinhold, "BONDO", QCPE Program No. 408, Indiana University, Bloomington, IN, 1980; J. E. Carpenter and F. Weinhold, unpublished work.

(38) On the basis of their similarly poor chlorine electron affinities, one would expect, however, that the semiempirical methods should give results analogous to RHF/STO-3G, where R_3 is 3.49 Å. The fact that C–Cl_c remains nearly covalent while the Cl–Cl distance shrinks to near covalency is probably due to the partial neglect of Pauli repulsions (through the NDO approximation) at Cl_c.

(39) R. Weiss and J. Macheleid, to be submitted for publication.

the geometries of CCl_3^+ (planar) and CCl_4 (tetrahedral) at the INDO level, obtaining bond lengths of 1.629 and 1.697 Å, respectively. Keeping these monomer geometries fixed, we then optimized two CCl_3^+/CCl_4 complexes. The first, of C_{3v} symmetry with the out-of-plane carbon p orbital of CCl_3^+ in line with the proximate C–Cl bond of CCl_4 in the arrangement $Cl_3C^+\cdots Cl$–CCl_3, was found to have an optimum $C\cdots Cl$ distance of 1.97 Å, with a binding energy of 30.5 kcal/mol and a transfer of charge to CCl_3^+ of 0.225e. The second, of C_{2v} symmetry with facing collinear C–Cl bonds in the arrangement Cl_2C–$Cl^+\cdots Cl$–CCl_3, was found to have an optimum $Cl\cdots Cl$ distance of 2.35 Å with a binding energy of 5.2 kcal/mol and a transfer of charge to CCl_3^+ of only 0.029e. Although the strength of binding in both of these complexes is likely to be overestimated by perhaps a factor of 2 or more, these results give support to the hypothesis that complexation of CCl_3^+ by CCl_4 will make it considerably easier for Cl^- to attack at one of the three chlorine atoms of CCl_3^+ rather than at the carbon atom.

As further illustration of this point, we considered a C_{3v} complex of CCl_3^+ with two molecules of CCl_4 in the arrangement Cl_3C–$Cl\cdots CCl_3^+\cdots Cl$–$CCl_3$, by adding another CCl_4 on the other face of the cation. We found the optimal $C\cdots Cl$ distances to both be 2.01 Å, resulting in a total binding energy of 54.7 kcal/mol and a charge transfer to CCl_3^+ of 0.328e. It is interesting to note that the occupancy of the out-of-plane carbon p orbital in CCl_3^+ decreases upon formation of this complex (from 0.69 to 0.62) and that the charge is effectively transferred from the CCl_4 molecules into the out-of-plane chlorine 3p orbitals, which gain in occupancy from 1.77 to 1.90.

IV. Conclusion

We have found that the trichlorocarbenium chloride species represents a local minimum at the RHF/6-31G* level of theory and that this species is not adequately described unless large basis sets are used and electron correlation is included. The longevity of such a species, relative to decomposition to the normal T_d isomer of CCl_4, should be enhanced by solvation of CCl_3^+ in CCl_4 under the experimental radiolysis conditions. We have shown the importance of n–σ^* charge transfer in stabilizing this ion pair. We conclude that such contact ion pairs are plausible sources of the transient 500-nm absorbance of CCl_4 pulse radiolysis[40] and

warrant further ab initio investigation. No conclusions should be drawn from the search by Gremlich et al.[10] for a stable C_{3v} contact ion pair using the STO-3G basis set, since the geometries searched did not allow for the type of n–σ^* complex considered here and the chosen basis set is inadequate to describe such a complex (chlorine electron affinity of the wrong sign). Thus, it no longer seems necessary to postulate a solvent-separated ion pair as the source of the 500-nm transient absorbance.

These findings are also relevant to the iodo compounds discussed in the Introduction. There are at least four factors that will cause an iodocarbenium iodide complex to differ from the chlorocarbenium chloride complex investigated here:

(1) The electron affinity of I is lower than that of Cl (71 vs. 83 kcal/mol), making I^- a better donor than Cl^-; this would allow the I–I bond in the complex to become more covalent and shorten its length.

(2) A C–I bond is weaker than a C–Cl bond, enhancing the n–σ^* stabilization of the complex due to a lower energy σ^* orbital.

(3) Iodine has a greater tendency than chlorine to form "hypervalent" compounds, due in part to its higher electropositivity (stronger polarization of σ^* toward iodine).

(4) Relativistic contraction of the valence 5s shell[41,42] may also lead to reduced steric repulsions between the two iodine atoms, allowing shorter I–I contacts.

From these considerations, it seems quite possible that the potential energy surface of R_2C–I–I contains only a single minimum, corresponding to a three-center, four-electron hypervalent species, in contrast to the nearly ionic Cl_2C–Cl–Cl species studied in this paper and in harmony with recent experimental findings of Weiss et al.[7]

Note Added in Proof. We have performed two additional calculations on the ion-pair **10**. The HF/6-31G* energy gradient was evaluated for **10**, confirming that the energy is optimal to within 10^{-5} au and that the structure is a true minimum. We also evaluated the full MP2/6-31G* energy for **10**, obtaining $-1\,876.284\,985$ au. This leads to a relative energy of the ion-pair **10** (with respect to isolated CCl_2 and Cl_2; see ref 29) of -17.2 kcal/mol at the MP2/6-31G* level, which compares favorably with the estimate (-16 kcal/mol) in Figure 2, and further strengthens the argument for the existence of the ion-pair isomer.

(40) A 500-nm transition corresponds to an excitation energy of 2.5 eV. The HOMO–LUMO transition in the ion pair is of $\pi \rightarrow \pi^*$ type, the HOMO being localized on Cl^- and the LUMO being localized on CCl_3^+. By Koopmans' theorem, the transition energy at the RHF/6-31G* level (from Table VI) is 0.216 au, or 5.9 eV. This value is much lower than the Koopmans' $\pi \rightarrow \pi^*$ transition energies in Cl_2C–Cl_2 and in isolated CCl_3^+ (which are 12.5 and 13.2 eV, respectively, at the RHF/6-31G* level) and could presumably be further reduced by correlation effects. Although these results tend to support our assignment, a more useful estimate of the expected excitation energy of the $CCl_3^+Cl^-$ complex would require direct study of the excited state.

(41) K. S. Pitzer, *Acc. Chem. Res.*, **12**, 271 (1979).
(42) P. Pyykkö and J. P. Desclaux, *Acc. Chem. Res.*, **12**, 276 (1979).