IR Matrix Spectroscopy of Pentachlorocyclopentadienyl Cation $C_5Cl_5^+$. Effect of Chlorine as a Substituent

Hrvoj Vančik,[*] Igor Novak,[†] and Davor Kiđemet

Department of Chemistry, Faculty of Science, University of Zagreb,
Strossmayerov trg 14, 10000 Zagreb, Croatia

Received: June 4, 1996; In Final Form: September 19, 1996[⊗]

The first direct observation of pentachlorocyclopentadienyl cation ($C_5Cl_5^+$) by IR spectroscopy was made in cryogenic SbF_5 matrix. The structure of the ion, analyzed by DFT calculations, was found to have D_{5h} symmetry. It was found that the stabilizing effect of chlorine lone pair electrons, which was observed in other α-chlorocarbocations (CCl_3^+ or $C_3Cl_3^+$), is not present in this molecule.

Introduction

Cyclopentadienyl cations have been prepared in the form of hexafluoroantimonate salts, but their structures were investigated only by ESR spectroscopy.[1] It was found that the ground state of pentachlorocyclopentadienyl cation **1** is a triplet with D_{5h} symmetry,[1a] exactly as predicted for this antiaromatic molecular ion. Five chlorine atoms bound to the ring of **1** may have a stabilizing effect.[1b] From our previous work[2a,b] as well as from Olah's NMR investigation of the trichloromethyl cation,[2c,d] it is known that α-chlorocarbocations are stabilized by back-donation of the chlorine lone pair electrons (α-*chloro effect*) via resonance forms **a** and **b** (Scheme 1).

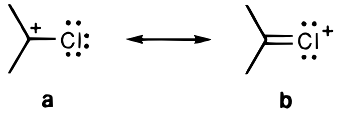
The partially double C−Cl bond in such cations is shorter compared with corresponding reference lengths in alkyl or aryl halides. Recent X-ray diffraction experiments made by Laube[1e] have shown that shortening of the C−Cl bond in α-chloro cations is 0.067 Å. Such a stabilization is also manifested in the upward shift of the C−Cl stretching frequency, which was observed in the IR spectra of simple α-chloroalkyl cations (for instance $\nu(\mathrm{C{-}Cl}) = 1045\ \mathrm{cm^{-1}}$ in CCl_3^+).[2a] The α-chloro effect in α-chloroalkyl cations is strong (because of the interaction between chlorine lone pairs and *vacant* C 2p orbital), but in the antiaromatic cation $C_5Cl_5^+$ (**1**) its significance may be modified because of interactions between Cl 3p and the *singly occupied* ring π-orbital.

In this work we wish to report a study of an α-chloro effect in cation **1** by analyzing the IR spectra with the aid of quantum chemical calculations. In addition, we shall compare the structure of this cation with its aromatic analogues, trichlorocyclopropenyl cation **2** and hexachlorobenzene **3** (Scheme 2).

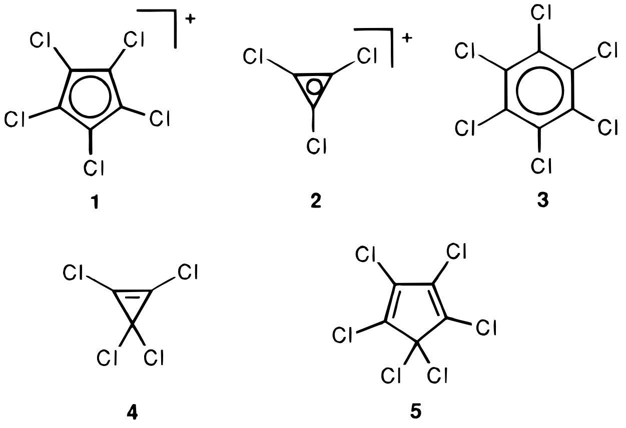
Results

SbF_5 Matrix Isolation. Cation **1** was prepared by reaction of hexachlorocyclopentadiene (**5**) and SbF_5 in the condensed phase. The precursor and a high excess of SbF_5 were codeposited[3] on the CsI window cooled to 70 K. The spectrum recorded at this temperature corresponded to the starting material. When the matrix was warmed to 150 K, a new sharp signal at 1401 $\mathrm{cm^{-1}}$ appeared in the spectrum (Figure 1). This spectrum remained unchanged even after the matrix was warmed up to 250 K. In a parallel experiment with $SbCl_5$ instead of SbF_5 the spectrum recorded at 150 K differs from that of the precursor but is much more complex.

SCHEME 1



SCHEME 2



Quantum Chemical Calculations. We performed density functional theory (DFT) calculations implemented in the *Gaussian 94* program.[4a] The hybrid B3-LYP functional[4b] and 6-31G** basis set were used in all calculations, since it was recently demonstrated[4c] that they can provide good values of vibrational frequencies for a large number of molecules.

Full geometry optimizations were performed for singlet (C_{2v}) and triplet (D_{5h}) cationic states (Figure 2). The calculations suggested that the triplet state was 31.8 kJ $\mathrm{mol^{-1}}$ more stable than the singlet. The calculated vibrational frequencies and relative intensities are given in Table 1. The corresponding DFT bar spectrum (Figure 3) shows that the singlet state should exhibit a much more complicated IR spectrum than the triplet, which has only two signals at 1338 and 752 $\mathrm{cm^{-1}}$, approximately.

Discussion

Assignment of the experimental spectrum was performed by comparison with the calculated spectra and with the spectra of other possible products of reactions between hexachlorocyclo-

---

[†] Department of Chemistry, National University of Singapore, Singapore 119260.

[*] To whom correspondence should be addressed. E-mail: vancik@olimp.irb.hr.

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1997.

S1089-5639(96)01610-6 CCC: $14.00

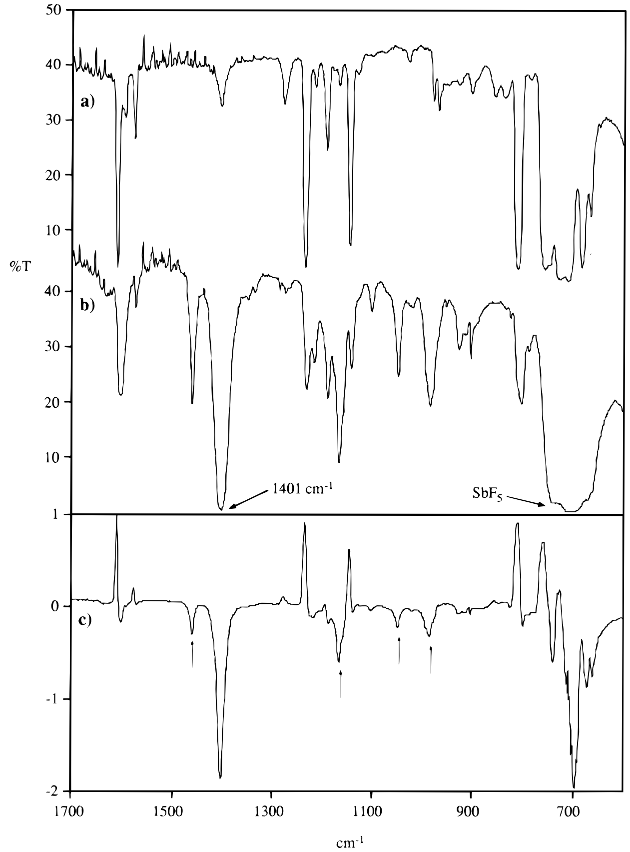


Figure 1. FTIR spectrum of C_5Cl_6 in SbF_5 matrix: (a) at 70 K; (b) at 150 K; (c) differential spectrum (C_5Cl_6 (up), $C_5Cl_5^+$ (down)). Unknown byproducts are labeled with arrows.

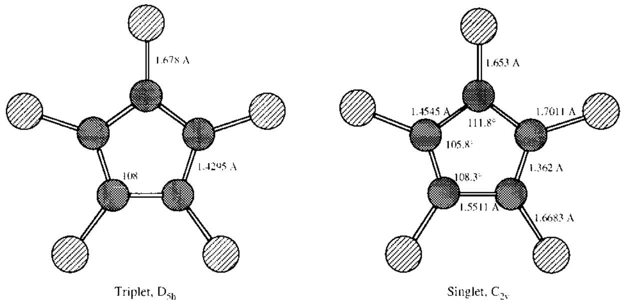


Figure 2. DFT optimized geometries of D_{5h} and C_{2v} $C_5Cl_5^+$ molecule.

TABLE 1: Observed and Calculated[a] IR Frequencies (cm^{-1}) and Relative Intensities (in Parentheses) of D_{5h} and C_{2v} Hexachlorocyclopentadienyl Cation

C_{2v}	D_{5h}	exptl
1592 (172)		
1559 (208)		
1316 (316)	1338 (654)	1401, vs
1188 (151)		
1159 (400)		
1023 (56)		
868 (301)		
768 (52)		
725 (117)	752 (81)	

[a] Calculated quantities are by DFT method.

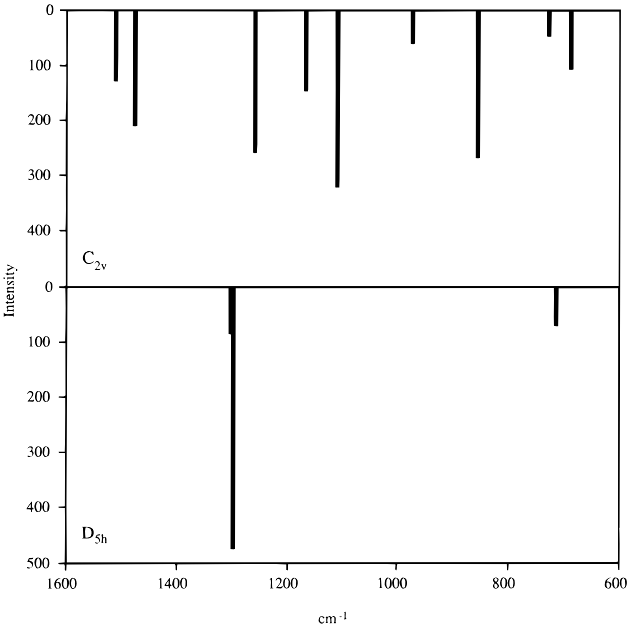


Figure 3. DFT calculated IR spectra of D_{5h} and C_{2v} $C_5Cl_5^+$ molecule.

TABLE 2: Comparison of DFT and Observed IR Frequencies (cm^{-1}) for $C_3Cl_3^+$ and C_6Cl_6 (Relative Intensities are in Parentheses)

molecule	exptl	calcd
C_6Cl_6	1346	1363 (191)
	1300	1272 (11)
		1223 (11)
	699	693 (78)
$C_3Cl_3^+$	1315	1339 (444)
	733	739 (33)

pentadiene and a strong Lewis acid. In most of these reactions hexachlorocyclopentadiene yields dimers and complexes, which were isolated previously[5] and whose spectra are very complicated, certainly much more than our spectrum, which exhibits only a single peak group at 1401 cm^{-1} (Figure 1b).

Another signal, predicted by the calculations to be at 752 cm^{-1}, is superimposed onto the SbF_5 vibrations and hence not clearly identifiable. This data strongly suggest that the spectrum in Figure 1b represents cation **1** in its triplet state (D_{5h} symmetry).

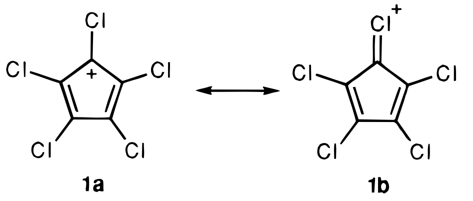
DFT calculations predict the existence of a single peak: 1338 cm^{-1} (degenerate ring deformation) in the 800−4000 cm^{-1} region. The experimental frequency is higher than the calculated one, but the DFT method may sometimes underestimate vibrational frequencies of some modes by up to 100 cm^{-1} as shown in the recent work[6a] on $C_5H_5^-$. In order to further demonstrate the suitability of DFT for analyzing the IR spectrum of $C_5Cl_5^+$, we present in Table 2 a comparison of experimental and DFT data for the related species $C_3Cl_3^+$ and C_6Cl_6.

The results show good agreement in terms of wavenumbers and also that wavenumbers of some modes can be underestimated at the B3-LYP/6-31G** level. The DFT molecular structure of the two species is also reproduced well compared to experimental results.[7] The maximum deviations of bond lengths and angles are less than 0.03 Å and 0.10°, respectively.

The experimental spectrum of **1** resembles the spectrum of hexachlorobenzene **3**, which is also simple, containing the dominant signal at 1346 cm^{-1} (ring deformation).[6b] The similarity between the spectra of **1** and **3** may suggest a similar influence of α-chloro substituents on the electronic structure and vibrational modes. Absence of the increased C−Cl stretching frequency (typical of α-chloroalkyl cations) in the spectrum of **1** indicates that back-donation of the chlorine lone pair electrons is small or negligible.

On the other hand, the IR spectrum of trichlorocyclopropenyl cation **2** is very different[7] and exhibits a 44 cm^{-1} increase in C−Cl stretching mode compared to the neutral precursor molecule[8] C_3Cl_4 (**4**). Although this shift in C−Cl stretching frequency is not as pronounced as in CCl_3^+ (200 cm^{-1}), it could

SCHEME 3



indicate the presence of the α-chloro effect, which can also be inferred from the relatively high C−Cl stretching force constant of 2.99 mdyn/Å. For comparison, the corresponding force constant in hexachlorobenzene (**3**) has much lower value of 2.30 mdyn/Å.[1b]

Back-donation of chlorine lone pair electrons leads to the shortening of C−Cl bonds. The C−Cl distance in **1** (D_{5h}) (1.678 Å) is only 0.025 Å shorter than the single C(sp^2)−Cl bond in hexachlorocyclopentadiene **5** (1.7027 Å),[9] i.e., the difference is more than 2 times smaller than Laube's value (0.067 Å). Such a small variation in the C−Cl distance supports the previous conclusion that the α-chloro effect is negligible in ion **1**. On the other hand, the effect was observed in cation **2** [7] where the C−Cl bond length of 1.631 Å is considerably shorter than that of its precursor **4** (the C(sp^2)−Cl bond in **4** is 1.684 Å). This change (0.053 Å) is close to Laube's value of 0.067 Å, which is typical for the α-chloro effect.

However, the α-chloro effect, described by resonance form **1b** (Scheme 3), could be predicted for the singlet structure of **1** (C_{2v}). Here, the central C−Cl bond should be shorter than the other four bonds, in agreement with our calculations (1.653 Å, Figure 1). The calculated value is close to the measured C−Cl distance in cation **2** (1.631 Å). This change in C−Cl distance on going from **5** (1.7027 Å) to **1** (C_{2v}) is 0.050 Å, i.e., in agreement with Laube's experimental results.

Conclusion

The pentachlorocyclopentadienyl cation can be prepared in a cryogenic SbF_5 matrix at 150 K and characterized by intense absorption at 1401 cm^{-1}. In the simulated IR spectrum based on the triplet ground state structure (D_{5h}) the most intense signal was calculated at 1338 cm^{-1}. The absorptions of C−Cl stretching vibrations were not observed in the spectrum above 800 cm^{-1}, but in the calculated spectrum they appear at 752 cm^{-1}. Absence of the increased C−Cl stretching signal (i.e., above 900 cm^{-1}) means that the chlorine−carbon bond is not strengthened by back-donation of the chlorine n-electrons (an α-*chloro effect*). A similar conclusion follows also from the calculated geometry of **1** (D_{5h}). Cation **1** thus does not appear to be stabilized by chlorine n-electrons, in contrast to its aromatic analogue trichlorocyclopropenyl cation **2**.

Experimental

The ion **1** was prepared from hexachlorocyclopentadiene provided by Merck-Schuchardt (zur Synthese) and distilled in vacuo. Antimony(V) fluoride (Merck-Schuchardt) was freshly distilled immediately before the deposition. Antimony(V) chloride was provided by Fluka. All IR spectra were recorded on a Perkin-Elmer 1725× FTIR spectrometer with 2 cm^{-1} resolution (100 scans). All the matrices were prepared on a CsI window cooled by a closed cycle cryostat ROK 10-300 Leybold Heraeus connected to vacuum line equipped with an oil diffusion pump. During the deposition, the temperature was held at 70 K and vacuum at 10^{-5} Torr. The flow of the sample was regulated by a Teflon valve. The deposition times were 10 min in all experiments. The matrix material (SbF_5 or $SbCl_5$) to sample ratio was estimated to be 500:1.

Acknowledgment. This work has been supported by the Ministry of Science of Croatia and Research Grant RP940601 from the National University of Singapore.

References and Notes

(1) (a) Breslow, R.; Chang, H.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1967**, *89*, 1112. (b) West, R. *Acc. Chem. Res.* **1970**, *3*, 130. (c) Olah, G. A.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1989**, *111*, 8020. (d) Olah, G. A.; Rasul, G.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1996**, *118*, 3580. (e) Laube, T.; Bannwart, E.; Hollenstein, S. *J. Am. Chem. Soc.* **1993**, *115*, 1731.

(2) (a) Vančik, H.; Percač, K.; Sunko, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 7418. (b) Vančik, H.; Percač, K.; Sunko, D. E. *J. Chem. Soc., Chem. Commun.* **1991**, 807.

(3) (a) Vančik, H. *Pure Appl. Chem.* **1995**, *67*, 761. (b) Vančik, H.; Sunko, D. E. *J. Am. Chem. Soc.* **1989**, *111*, 3742.

(4) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1995. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391.

(5) (a) Fritz, H. P.; Schäfer, L. *J. Organomet. Chem.* **1964**, *1*, 318. (b) Mark, V.; Weil, E. D. *J. Org. Chem.* **1971**, *36*, 676. (c) Newcomer, J. S.; McBee, E. T. *J. Am. Chem. Soc.* **1949**, *71*, 946. (d) McBee, E. T.; Smith, D. K. *J. Am. Chem. Soc.* **1955**, *77*, 389. (e) Newcomer, J. S.; McBee, E. T. *J. Am. Chem. Soc.* **1949**, *71*, 952.

(6) (a) Berces, A.; Ziegler, T.; Fan, L. *J. Phys. Chem.* **1994**, *98*, 1584. (b) Vapor Phase. *The Aldrich Library of FTIR Spectra*, Edition I; Aldrich Chemical Co.: Milwaukee, 1989; p 949.

(7) (a) Clark, G. R.; Taylor, M. J.; Steele, D. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3597. (b) Mair, H. J.; Bauer, S. H. *J. Phys. Chem.* **1971**, *75*, 1681.

(8) Adame, I. E.; Vicharelli, P. A.; Schwartz, M. *Spectrochim. Acta* **1981**, *37A*, 847.

(9) Chang, C. H.; Bauer, S. H. *J. Phys. Chem.* **1971**, *75*, 1685.