COMMENTS

Comment on “IR Matrix Spectroscopy of Pentachlorocyclopentadienyl Cation $C_5Cl_5^+$”

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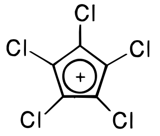
In previous paper[1] we have investigated the effect of chlorine on the stabilization of antiaromatic (D_{5h}) $C_5Cl_5^+$ ion **1**. We have found that shortening of the C−Cl bond by 0.025 Å caused by chlorine *n*-electron back-donation is not as significant as in nonaromatic C_{2v} structure **2** (0.050 Å). Here we describe the isolation and the structure of related cation **3** obtained by replacement of one chlorine with hydrogen. The ion was isolated starting from 1,2,3,4,5-pentachlorocyclopentadiene[2] in SbF_5 matrix under the same experimental conditions as in the previous work. Its IR spectrum (Figure 1, Table 1) agrees with the frequencies and intensities calculated by density functional theory at the B3-LYP/6-31G**[3] level. Major disagreement can be observed in signals at 1446 and 1168 cm^{-1} because signals in this spectral region are somtimes underestimated by DFT.[1b] The calculations included full geometry optimization. Both singlet and triplet C_{2v} structures of $C_5Cl_4H^+$ were found to be minima. However, the singlet is 1.1 kcal mol^{-1} more stable. As can be seen from frequencies and intensities in Table 1, the singlet structure agrees much better with the experimental data. The dominant experimental signal at 1627 cm^{-1} is not predicted in the spectrum calculated for the triplet structure. It could be that solid superacid medium has an additional effect on the stabilization of singlet structure.



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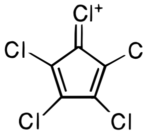

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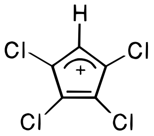

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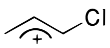

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Typical absorbances at 1627 and 1397 cm^{-1} correspond to the C═C stretching vibration of the alkene substructure and allylic CCC^+ asymmetric stretching vibration of the allyl cation substructure, respectively. Most of the polychlorinated allyl cations have CCC^+ stretching signals in this spectral region.[4]

The extent of the chlorine *n*-electron back-donation is demonstrated by calculated geometry parameters and Mulliken atomic charge distribution (Figure 2). The ion **3** has topology in which π-electrons are distributed in two fragments, dichloroalkene and dichloroallyl cation. The C−Cl bond length in the allyl substructure of **3** (1.663 Å) is close to the C−Cl distance previously calculated for the parent *cis*-1-chloroallyl cation **4** (1.640 Å).[5] Both values are lower in comparison with the expected C−Cl bond length in neutral chloroalkenes (1.700 Å).

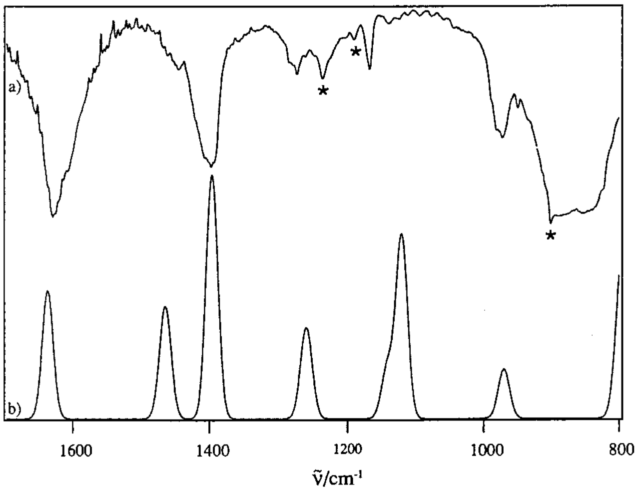

Figure 1. Experimental (top) and calculated (B3-LYP/6-31G**)[3] spectrum of **3** (singlet). Unknown impurities are labeled with stars.

TABLE 1: Experimental and Calculated (B3-LYP/6-31G)[3] IR Frequencies and Intensities[a]**

exptl	calcd B3-LYP/6-31G** singlet	calcd B3-LYP/6-31G** triplet
1627 s	1634 (154)	
1446 m	1486 (183)	1440 (262)
1397 vs	1382 (418)	1385 (249)
1272 m	1259 (81)	1343 (92)
	1145 (26)	1304 (265)
1168 s	1120 (311)	1147 (133)
973 m	971 (26)	982 (53)
	811 (153)	

[a] The appropriate scaling factor for harmonic frequencies was taken from ref 3c.

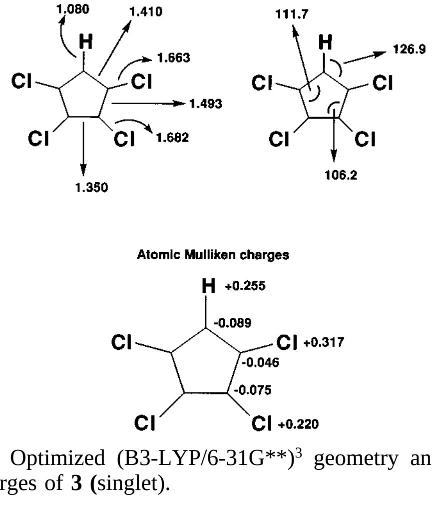

Figure 2. Optimized (B3-LYP/6-31G**)[3] geometry and Mulliken atomic charges of **3 (**singlet).

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Such a shortening of carbon−chlorine bonds in both the cations is a consequence of the chlorine *n*-electron back-donation. Accordingly, chlorines bound to terminal allyl cation carbon atoms in **3** are more positive (+0.317) than chlorines bound to the alkene substructure (+0.220) (Figure 2). The calculated distribution of π-electrons which is responsible for the C_{2v} symmetry of **3** is optimal because halogen *n*-electron stabilization in allyl cations is more pronounced if chlorines are bound to terminal carbon atoms.

References and Notes

(1) (a)Vančik, H.; Novak, I.; Kidemet, D. *J. Phys. Chem. A* **1997**, *101*, 1523. (b) Ibid; see ref 6a.

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