Electron Spin Resonance Spectra and Structure of the Radical Cations of 1,3-Dichloropropane and Other Dichloroalkanes

Akinori Hasegawa *
Department of Chemistry, Kogakkan University, Ise-shi 516, Japan
Martyn C. R. Symons
Department of Chemistry, The University, Leicester LE1 7RH
Masaru Shiotani
Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724, Japan

Exposure of a dilute solution of 1,3-dichloropropane in Freon to *X*-rays at 77 K gave e.s.r. spectra composed of many lines, which are attributable to hyperfine coupling to two equivalent chlorine nuclei and two equivalent protons in the corresponding cation. Similar experiments with methyl-substituted compounds revealed that the two equivalent protons can be assigned to one of the protons in each terminal methylene group. CNDO/2 calculations for the radical cation suggest that reasonable values for the coupling constants of these two protons are obtained for a specific non-planar cyclic structure having a Cl–Cl three-electron bond $(\sigma_1{}^2\sigma_2{}^1)$. E.s.r. spectra were also studied for the radical cations of other dichloroalkanes, $\mathrm{Cl(CH_2)}_n\mathrm{Cl}$. For $n = 1$, 2, 4, and 5, these also gave spectra indicating a SOMO on two equivalent chlorine nuclei.

The authors have previously reported the radical cations of halogenoalkanes[1] formed in Freon matrices which have been shown to stabilize radical cations.[2] When dilute solutions of chloroethane or bromoethane in $\mathrm{CCl_3F}$ were exposed to *X*-rays at 77 K, the corresponding radical cations formed weak σ^* bonds between the halogen atom and one chlorine atom of the solvent, $[\mathrm{Rhal}\dot{-}\mathrm{ClCFCl_2}]^+$. For the cation of iodoethane, no clear evidence for such bonding was obtained. On the other hand, exposure of more concentrated solutions of these halogenoalkanes yielded dimer cations, $[\mathrm{Rhal}\dot{-}\mathrm{halR}]^+$.

For the analysis of the e.s.r. spectra for $[\mathrm{RCl}\dot{-}\mathrm{ClCFCl_2}]^+$ and $[\mathrm{RBr}\dot{-}\mathrm{ClCFCl_2}]^+$, an approximately axially symmetric *g* tensor was assumed since the central parts of the spectra were poorly defined. For the iodoethane cation at 4 K, a clearly rhombic *g* tensor was obtained. When the radical cation of bromoethane was reinvestigated at 4 K, the *g* tensor was confirmed to be rhombic and one more *g* value was added to the two values originally reported.[3]

One of the present authors has also reported that a hole is shared in the atomic orbitals of two bromine atoms for the radical cations of $\mathrm{CH_2Br_2}$, $\mathrm{CHBr_3}$, and $\mathrm{CBr_4}$.[4] Accordingly, exposure of solutions of Freon containing dihalogenoalkanes with terminal halogen atoms was investigated. Many dichloroalkanes gave e.s.r. spectra suggesting the presence of two equivalent chlorine atoms. In particular, a well defined spectrum was obtained for the $[\mathrm{Cl(CH_2)_3Cl}]^{+\bullet}$ cation and the structure of this cation is discussed in detail in this paper.

Experimental

A range of dichloroalkanes, including 1,3-dichloropropane, were purchased from Tokyo Kasei Co. Solutions of these dichloroalkanes, in concentrations less than 1% vol, in 1,1,2-trichloro-1,2,2-trifluoroethane ($\mathrm{CCl_2FCClF_2}$), trichlorofluoromethane ($\mathrm{CCl_3F}$), or tetrachloromethane ($\mathrm{CCl_4}$) were frozen in Spectrosil e.s.r. tubes and exposed to *X*-rays (Cu target, 40 kV, 20 mA) for 3 h at 77 K. E.s.r. spectra were measured at 77 K and at various temperatures on a JEOL JES-FE1XG spectrometer.

Table 1. E.s.r. parameters for the $[\mathrm{Cl(CH_2)_3Cl}]^{+\bullet}$ radical cation formed in $\mathrm{CCl_2FCClF_2}$

g Tensor				Hyperfine tensor (G)[a]		
g_x	g_y	g_z	Nuclei	A_x	A_y	A_z
~2.04,	~2.02,	1.998	2 ^{35}Cl	~15,	~15,	95
			(^{37}Cl	~12,	~12,	79)[b]
			2 ^{1}H	~22,	~22,	22.3

[a] $\mathrm{G} = 10^{-4}$ T. [b] There are three pairs of ^{35}Cl–^{35}Cl, ^{35}Cl–^{37}Cl, and ^{37}Cl–^{37}Cl with the relative amounts of 1:0.65:0.10, for two equivalent Cl nuclei.

Results and Discussion

The Radical Cation of 1,3-*Dichloropropane.*—Exposure of a dilute solution of $\mathrm{Cl(CH_2)_3Cl}$ in $\mathrm{CCl_2FCClF_2}$ to *X*-rays at 77 K gave the e.s.r. spectrum shown in Figure 1. The spectrum has the parallel (*z*) features composed of groups of seven major lines, indicating the presence of two equivalent Cl nuclei with nuclear spins of 3/2. Thus, the formation of the $[\mathrm{Cl(CH_2)_3Cl}]^{+\bullet}$ radical cation was suggested. Since chlorine has the two isotopes of ^{35}Cl ($I = 3/2$, 75.4%) and ^{37}Cl ($I = 3/2$, 24.6%) with the relative magnetogyric ratios of 1:0.832, there are three pairs of ^{35}Cl–^{35}Cl, ^{35}Cl–^{37}Cl, and ^{37}Cl–^{37}Cl with the relative amounts of 1:0.652:0.105, in the case of two equivalent Cl nuclei. Although the outermost groups in the spectrum are partly masked by intense lines for hydrogen atoms, they can be satisfactorily interpreted only when each of the outermost lines due to the three isotope-pairs is assumed to split into a 1:2:1 triplet. As can be seen in Figure 1, excellent agreement was obtained between the features in the spectrum and the stick diagrams calculated by a strict matrix-diagonalization for the two equivalent Cl nuclei and two doublets with the e.s.r. parameters listed in Table 1. Upon the calculation of the stick diagrams, unequal g_x and g_y tensor elements were used because rhombic *g* tensors have been revealed in the cases of $[\mathrm{C_2H_5Br}\dot{-}\mathrm{ClCFCl_2}]^+$ and $\mathrm{C_2H_5I}^{+\bullet}$.[1,3] However, their components are so poorly resolved that their assignments may contain some errors. E.s.r. observation at various temperatures showed that the spectrum

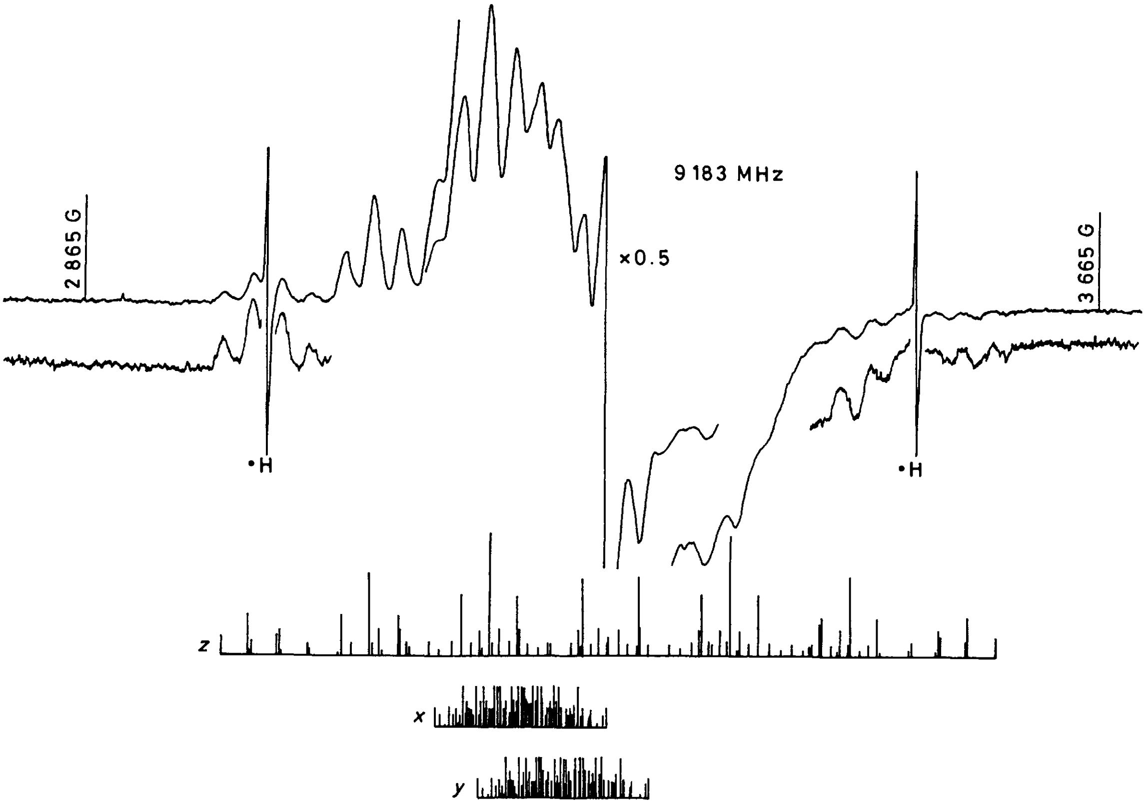

Figure 1. First-derivative X-band e.s.r. spectrum of a dilute solution containing $Cl(CH_2)_3Cl$ in CCl_2FCClF_2 after exposure to X-rays at 77 K. The stick diagrams show the line positions and line intensities calculated for the $[Cl(CH_2)_3Cl]^{+\cdot}$ radical cation with the parameters listed in Table 1

assigned to the cation decayed at 118 K without any significant spectral change, although other unassigned lines remained in the central part of the spectrum up to a higher temperature.

An e.s.r. spectrum similar to that in Figure 1 was also observed at 77 K for solutions in CCl_3F, which indicates that the two additional nuclei are protons in the $[Cl(CH_2)_3Cl]^{+\cdot}$ cation and not ^{19}F nuclei from matrix molecules. However, exposure of a solution of $Cl(CH_2)_3Cl$ in CCl_4, unfortunately, yielded only $^{\cdot}CCl_3$ and $CCl_4^{+\cdot}$ radicals.[5,6] For the assignment of the protons, solutions of available methyl-substituted compounds in CCl_2FCClF_2 were exposed to X-rays at 77 K. Similar spectra with slightly larger line widths were obtained for both $ClCH_2C(CH_3)_2CH_2Cl$ and $CH_3ClCH(CH_2)_2Cl$, suggesting that the two equivalent protons in the $[Cl(CH_2)_3Cl]^{+\cdot}$ radical cation are not the protons bonded to the central carbon atom but one from each terminal CH_2Cl group.

E.s.r. parameters for $[Cl(CH_2)_3Cl]^{+\cdot}$ are listed in Table 1. When spin densities on each chlorine (^{35}Cl) nucleus were calculated from the observed hyperfine coupling constants, a = 42 G and $2B$ = 53 G, and the atomic values, a° = 1 666.0 G and $2B^{\circ}$ = 100.68 G,[7] they indicated that a 'hole' is largely and equally shared by the $3p$ orbitals of the two chlorine nuclei in the cation.

The magnitude of the observed hyperfine coupling constants for the two protons, 22.3 G, may be the key to determining the structure of the radical cation. Semi-empirical MO calculations were performed for the $[Cl(CH_2)_3Cl]^{+\cdot}$ cation by a CNDO/2 method. Geometrical optimization gave the non-planar conformation shown as **structure 1** in Figure 2, where the distance between the two chlorine atoms is short (1.725 Å) and these two atoms and the three carbon atoms make a five-membered ring. However, only the H(2) atom in **structure 1** is predicted to give a large proton coupling constant, which is inconsistent with the experimental result of large coupling constants for two equivalent protons.

Regarding the conformation of a neutral parent $Cl(CH_2)_3Cl$ molecule, i.r. spectroscopic studies have revealed that the molecule in the crystalline solid state prefers the *gauche–gauche* conformation which can be obtained by clockwise internal rotations of 120° from the *trans* conformation.[8] Therefore, the relaxation process for the radical cation after the capture of a hole was investigated by the CNDO/2 method, using the same C–C, C–Cl, and C–H bond lengths as those obtained for the optimized **structure 1**, but adjusting the C–C–C bond angle. These calculations led us to conclude that internal rotation is induced to decrease the distance between the two chlorine atoms, and to relax the cation *via* a planar conformation (**structure 2**) to the optimized **structure 1**, as shown in Figure 3. Although the total energy of **structure 2** is close to that of **structure 1**, the large C–C–C bond angle in **structure 2** seems to reflect a strain from the planar conformation and no proton gives a large coupling constant.

On the other hand, conformations with rotation angles slightly smaller than in the case of **structure 2**, in other words, with small rotation angles for the CH_2Cl groups in opposite phase in reference to the planar conformation, gave a large coupling constant to one of the two protons in each terminal CH_2Cl group, as shown in Figure 3. **Structure 3** with a rotation angle of 15° in the opposite phase, has the two protons H(3), H(6) which are close to the plane containing the three carbon atoms and give coupling constants of 16.9 G. This is reasonably close to the observed value 22.3 G. For this conformation, the C–C–C bond angle is almost equal to the tetrahedral angle and the Cl–Cl bond length is the shortest among these three rotation isomers. Unfortunately, the total calculated energy for this conformation is not the lowest, as shown in Figure 3. It is

Structure 1

Atoms	^{1}H coupling (G)[a]
H(1)	0.8
H(2)	16.7
H(3)	7.1
H(4)	5.3
H(5)	7.1
H(6)	5.3

Structure 2

Atoms	^{1}H coupling (G)
H(1)	7.8
H(2)	7.8
H(3)	6.0
H(4)	6.0
H(5)	6.0
H(6)	6.0

Structure 3

Atoms	^{1}H coupling (G)[a]
H(1)	5.7
H(2)	5.7
H(3)	16.9
H(4)	0.3
H(5)	0.3
H(6)	16.9

[a] G = 10^{-4} T.

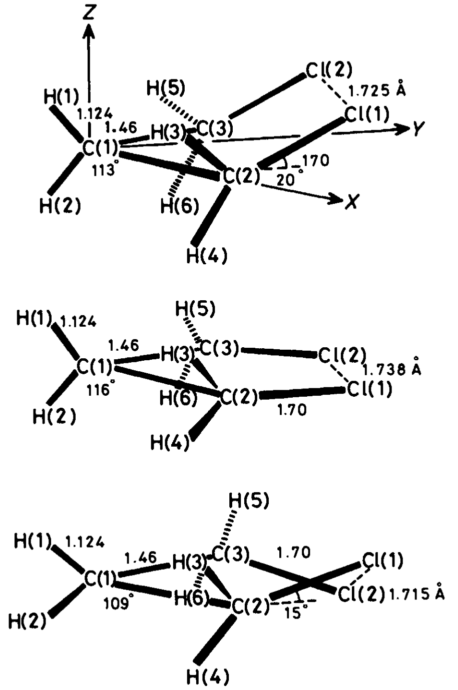

Figure 2. Rotational isomers for the $[Cl(CH_2)_3Cl]^{+\cdot}$ radical cation and the coupling constants in G (G = 10^{-4} T) calculated for their protons by a CNDO/2 method. **Structure 1** has the optimized geometry, and **structure 2** is planar. **Structure 3** has a conformation acquired in the relaxation process of the radical cation, and this structure was proposed for the radical cation. Unless otherwise noted, tetrahedral angles were assumed

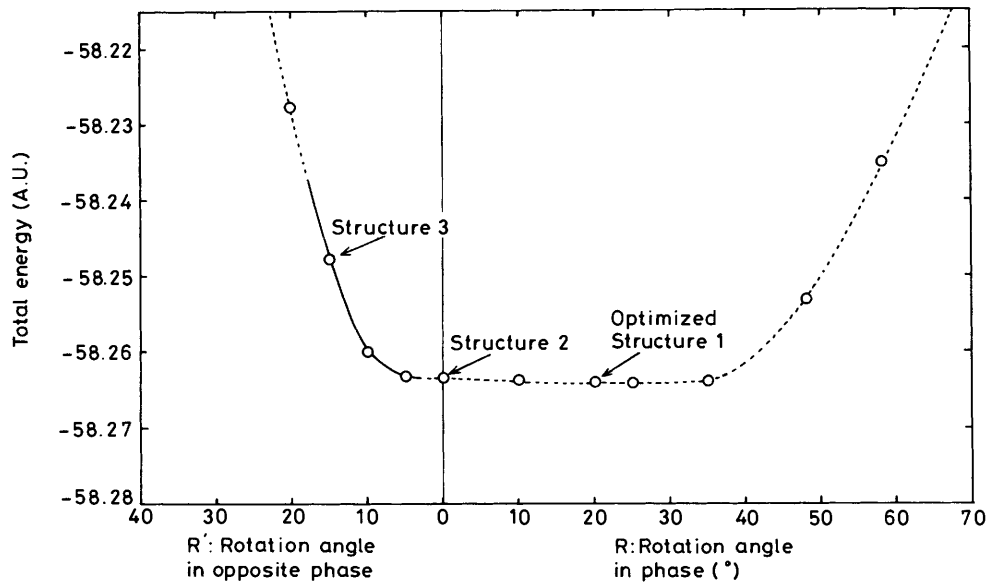

Figure 3. Change of total energy for the $[Cl(CH_2)_3Cl]^{+\cdot}$ radical cation *vs.* the internal rotation angle for the CH_2Cl groups, R′ rotations in phase and R″ rotations in opposite phase in reference to the planar conformation (see Figure 2). Calculation was performed by a CNDO/2 method. Conformations in the region indicated with the solid line gave a large coupling constant to one of the two protons in each terminal group

noteworthy that semi-empirical calculations do not always provide correct results for the determination of conformation.[9] Therefore, it may be plausible to assign the conformation of the $[Cl(CH_2)_3Cl]^{+\cdot}$ radical cation to **structure 3**.

There may be a criticism for the use of the CNDO/2 method giving results which are somewhat in error, especially for proton hyperfine coupling constants. However, as far as discussion is limited to the approximate magnitude of the couplings for the protons giving the largest couplings, the number of the protons, and the positions of the protons in the cation, the conclusion derived from the discussion may be reliable.

Distribution of spin densities for this conformation is listed in Table 2. These suggest that the unpaired electron is primarily in the 3*d* orbitals rather than the 3*p* orbitals on the two chlorine atoms. This result is contrary to a chemical intuition and does not agree with the e.s.r. data. It may be caused by the selection of the co-ordination system used for the calculation or may be resulted from the limit of the CNDO/2 method. In fact, for the

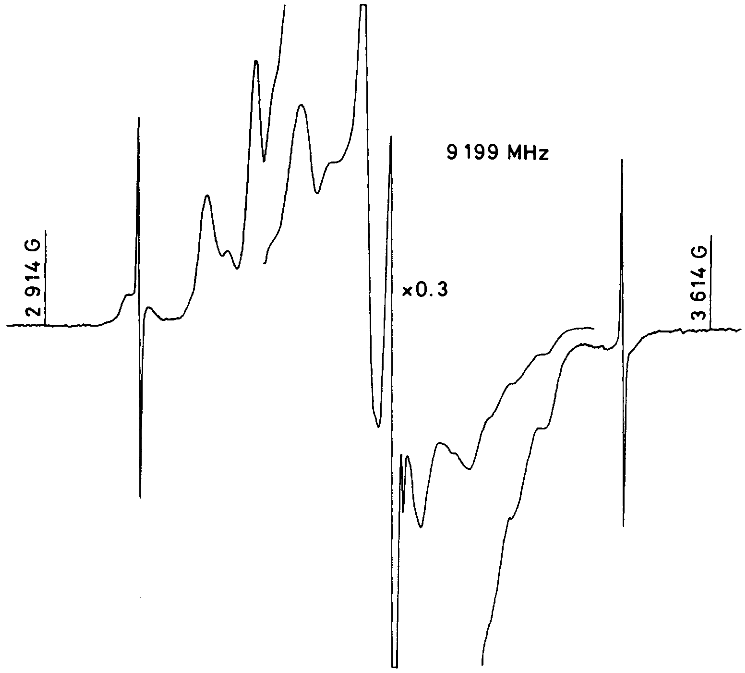

Figure 4. First-derivative *X*-band e.s.r. spectrum of a dilute solution containing $Cl(CH_2)_2Cl$ in CCl_2FCClF_2 after exposure to *X*-rays at 77 K, showing features assigned to the $[Cl(CH_2)_2Cl]^{+\cdot}$ radical cation

Table 2. Distribution of spin densities on the $[Cl(CH_2)_3Cl]^{+\cdot}$ radical cation in **structure 3**, calculated by a CNDO/2 method[a]

Atoms		Spin densities	Atoms	Orbital Spin densities	
C(1)	$2s$	−0.0014	Cl(1)	$3s$	0.0054
	$2p_Z$	−0.0041		$3p_Y$	−0.0183
C(2)	$2s$	0.0081		$3d_{X^2-Y^2}$	0.3072
	$2p_Y$	0.0935	Cl(2)	$3s$	0.0054
C(3)	$2s$	0.0081		$3p_Y$	−0.0274
	$2p_X$	0.0568		$3d_{X^2-Y^2}$	0.1468
	$2p_Y$	0.0569		$3d_{XY}$	0.1664
H(1)	$1s$	0.0112	H(4)	$1s$	0.0006
H(2)	$1s$	0.0112	H(3)	$1s$	0.0006
H(3)	$1s$	0.0033	H(6)	$1s$	0.0333

[a] The *x,y,z* co-ordination system shown in Figure 2 was used.

$[Cl(CH_2)_2Cl]^{+\cdot}$ cation, similar calculations showed that $3p$ orbitals are used in this case (see below).

Radical Cations of Other Dichloroalkanes.—A septet of lines was obtained in the e.s.r. spectra of solutions of dichloroalkanes $Cl(CH_2)_nCl$ (n = 1, 2, 4, and 5) in CCl_2FCClF_2, indicating that the cationic centre is again localized on the two chlorine atoms. However, they were not observed for dichloroalkanes with longer hydrocarbon chains, *e.g.* n = 8 or 10. Spectral lines for $[CCl_2H_2]^{+\cdot}$ are broad probably because of unresolved ^1H coupling, whilst the spectrum assigned to $[Cl(CH_2)_2Cl]^{+\cdot}$ is well defined, as shown in Figure 4. Although $A_{max.}(Cl)$ can be measured to be almost equal to the $A_z(Cl)$ value for $[Cl(CH_2)_3Cl]^{+\cdot}$ no detailed analysis was attempted for this spectrum, because the axes of the hyperfine tensors of the two chlorine nuclei are not expected to be parallel, as will be shown later. On the other hand, the spectrum for $[Cl(CH_2)_4Cl]^{+\cdot}$ had narrower features showing a further splitting into several (four to five) lines with a mean separation of *ca.* 14 G. Again the spectrum is unfortunately too poorly defined to warrant further analysis. For the $[Cl(CH_2)_5Cl]^{+\cdot}$ cation, a broad spectrum was observed.

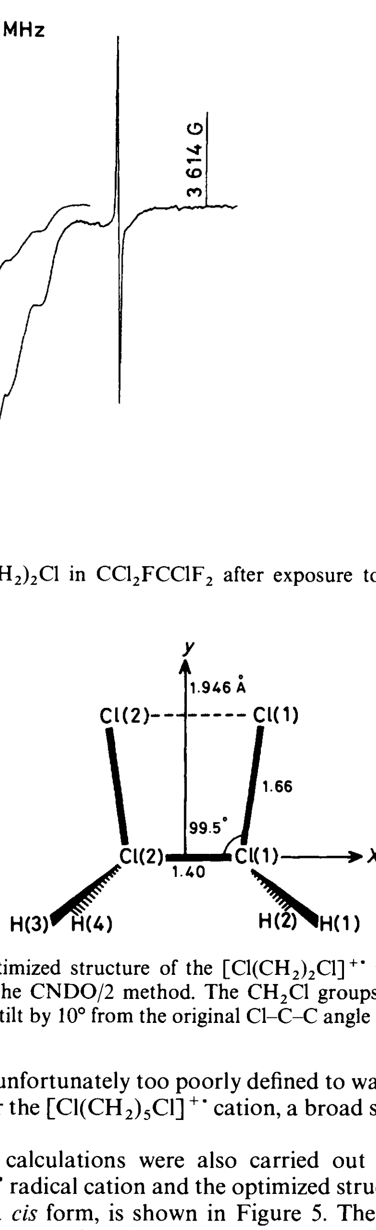

Figure 5. Optimized structure of the $[Cl(CH_2)_2Cl]^{+\cdot}$ radical cation, obtained by the CNDO/2 method. The CH_2Cl groups having tetrahedral angles tilt by 10° from the original Cl–C–C angle

CNDO/2 calculations were also carried out for the $[Cl(CH_2)_2Cl]^{+\cdot}$ radical cation and the optimized structure, having the expected *cis* form, is shown in Figure 5. The calculations indicate that the *cis* form is much more stable than the *trans* or *gauche* form. The CH_2Cl groups in the optimized structure tilt by 10° from the tetrahedral angle to reduce the distance between the two chlorine nuclei to 1.946 Å. In accord with the sharp spectrum observed, calculated spin densities on the protons are negligibly small (−0.0001). Using the co-ordination system for the calculations shown in Figure 5, the spin density matrix for $3p$ orbitals on chlorine has large off-diagonal elements. Therefore diagonalization was performed. This gave a spin density of 0.441 and the direction cosines (0.9609, −0.2769, 0.000), with regard to the *x,y,z* system shown in Figure 5, to the $3p$ orbital possessing the large spin density on the Cl(1) atom. The two $3p$ orbitals sharing the hole on the two chlorines are approximately aligned, with an angle of 32° between the two directions. This result, and the short distance between the two chlorine atoms, imply that a direct σ* bond is formed between the two chlorine atoms. The nature of the radicals—with the unpaired electron in a σ*-type orbital formed from 3*p* orbitals in the chlorines—suggests a close analogy with radicals such as $[R_3P\dot{-}PR_3]^+$,[10,11] $[R_2S\dot{-}SR_2]^+$,[12–15] and $[RS\dot{-}SR]^-$.[16] The σ* bond can also be represented as a three-electron bond $(\sigma_1{}^2\sigma_2{}^1)$. Deviation from the ideal 'linear' structure in this case arises because of a large strain caused by the planar four-membered ring. Similar cyclizations were also proposed for the cations of the other dichloroalkanes having features attributable to two equivalent chlorine nuclei. Presumably for the long-chain dichloroalkanes, the matrix prevents the large movement required for such cyclizations.

If this is the case, then surely a $B\cos^2\theta$ relationship (in modified form) would be expected to apply for the β-proton splittings for the terminal methylene groups. Two large splittings (for the formal five-membered ring) might then be predicted (given the shape indicated in **structure 3** of Figure 2), whereas the six-membered ring might well be expected to have fewer, smaller splittings. For $[Cl(CH_2)_2Cl]^{+\bullet}$, the appropriate angle θ is poor for interaction, and the strain in the ring would further reduce $a(CH_2)$, in line with observation.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 61470012) from the Japanese Ministry of Education, Science, and Culture.

References

1 G. W. Eastland, S. P. Maj, M. C. R. Symons, A. Hasegawa, C. Glidewell, M. Hayashi, and T. Wakabayashi, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1439.

2 M. C. R. Symons, *Chem. Soc. Rev.*, 1984, **13**, 393; M. Shiotani, *Magn. Reson. Rev.*, 1987, **12**, 333.

3 M. C. Symons, H. Muto, K. Toriyama, K. Nunome, and M. Iwasaki, *J. Chem. Soc., Perkin Trans. 2*, 1986, 2011.

4 M. C. R. Symons, *J. Chem. Res.*, 1985, (*S*), 256.

5 S. P. Mishra and M. C. R. Symons, *Radiat. Phys. Chem.*, 1975, **7**, 617.

6 M. C. R. Symons, E. Albano, T. F. Slater, and A. Tomasi, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 2205.

7 M. C. R. Symons, 'Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy,' Van Nostrand Reinhold Co., Berkshire, 1978.

8 J. K. Brown and N. Sheppard, *Proc. R. Soc., A*, 1955, **231**, 555.

9 H. Chandra, M. C. R. Symons, and A. Hasegawa, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 759.

10 T. Gillbro, C. M. L. Kerr, and F. Williams, *Mol. Phys.*, 1974, **28**, 1225.

11 A. Hasegawa, G. D. G. McConnachie, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 1005.

12 D. J. Nelson, R. L. Petersen, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1977, 2005.

13 R. L. Petersen, D. J. Nelson, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1978, 225.

14 D. N. O. Rao, M. C. R. Symons, and B. W. Wren, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1681.

15 X.-Z. Qin, O. Meng, and F. Williams, *J. Am. Chem. Soc.*, 1987, **109**, 6778.

16 M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1979, 1468.

Received 22*nd February* 1988; *Paper* 8/00714