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^{13}C HYPERFINE COUPLING AND STRUCTURE OF THE ·CHCl$_2$ RADICAL IN CH$_2$Cl$_2$ CRYSTAL BY ESR

Anders LUND and Yuhei SHIMOYAMA [*]

The Swedish Research Councils' Laboratory, Studsvik, Fack, S-611 01 Nyköping, Sweden

Measurement of the ^{13}C hyperfine coupling constant of ·CHCl$_2$ in single crystal CH$_2$Cl$_2$ at 77 K leads to the conclusion that the radical converts between two equivalent pyramidal structures at a rate significantly higher than 10^9 Hz. The anisotropy of the g-factor and the ^{1}H, ^{35}Cl and ^{13}C hyperfine couplings is consistent with an average planar structure. The conclusion is supported by ab initio calculations which show that the barrier for interconversion corresponds to a rate of the order 10^{13} Hz. A similar behaviour is predicted for ·CH$_2$Cl.

1. Introduction

Recent experimental studies have indicated that mono- and dichloro alkyl radicals have a planar structure [1–3]. This disagrees with theoretical results [4] which point to a pyramidal structure at least for the prototype radicals ·CH$_2$Cl and ·CHCl$_2$. In this paper we propose that rapid inversion of the pyramidal radicals can explain the difference in conclusions. This hypothesis is supported experimentally by the magnitude of the ^{13}C hyperfine splitting reported here for the ·CHCl$_2$ radical and theoretically [5] by the low barrier of inversion of the ·CH$_2$Cl and ·CHCl$_2$ radicals. On this basis it is concluded that the ·CHCl$_2$ converts between a pyramidal structure with a bending angle of +α (fig. 1)
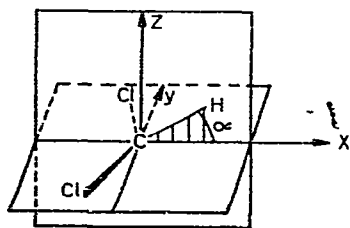

Fig. 1. Geometry of the ·CHCl$_2$ radical. Cl—C—Cl lies in the *xy* plane, CH in the *xz* plane.

[*] Present address: Department of Biophysics, University of Stockholm, Stockholm, Sweden.

to the equivalent structure with −α at a frequency which is significantly higher than the frequency of observation by means of electron spin resonance (ESR). Thus, the radicals appear to be planar on the ESR time scale. This inversion can be inferred from the magnitude of the ^{13}C splitting which is larger than expected for a rigid planar structure.

2. Experimental

Single crystals of CH$_2$Cl$_2$ contained in Suprasil tubes were irradiated with a ^{60}Co source at 77 K. For the measurement of ^{13}C satellite lines in single crystals the total dose was 5 Mrad. The method of making single crystals has been described [3]. ESR spectra were obtained at a microwave frequency of 9.15 GHz. The spectra described here were obtained after brief annealing of the samples at a temperature slightly below the melting point, a procedure that has previously [3] been found to increase the resolution. The measurements were primarily performed at 77 K. At a few orientations measurements were made at temperatures between 14 and 40 K using a helium variable temperature cryostat and at 133 K. The microwave power was 1 mW at and above 77 K, 2μW at and below 40 K. 100 kHz field modulation was employed.

3. Results

Satellite lines attributed to ^{13}C hyperfine interaction were observed at 77 K on the sides of the main spectrum of the CH_2Cl_2 single crystal. The angular variation of these lines was studied as the crystal was rotated about an axis which is the axis of the tube containing the crystal. The curves shown in fig. 2 support the previous conclusion [3] that site-splitting occurs. A similar angular variation was obtained for the g-factors of the two sites. One notes that the extremes of the anisotropic g-factor occur at the same orientations as for the ^{13}C splitting. An example of a spectrum showing a maximum in the ^{13}C splitting for one of the sites is shown in fig. 3. Probably because of spectral overlap with the main spectrum, the ^{13}C lines were not seen at all crystal orientations, e.g. parallel to the tube axis.

The ^{13}C splitting is assumed to be axially symmetric with $0 < A_\perp < A_\parallel$. With this assumption the minimum coupling in a rotation plane equals $A_\perp$. The minimum ^{13}C splitting of fig. 2 gives $A_\perp = 58$ G. The maximum is 115 G. This gives $A_\parallel \geqslant 115$ G. We have the following equations

$$A_\parallel = a + 2b \geqslant 115, \qquad A_\perp = a - b = 58,$$

with the solutions $a \geqslant 77$ G, $b \geqslant 19$ G.

The value of a (^{13}C) is larger than expected for a planar radical ($\cdot CH_3$ has $a(^{13}C) = 38$ G [6]) indicating that $\cdot CHCl_2$ is nonplanar. The $\cdot CCl_3$ radical has $a(^{13}C)$
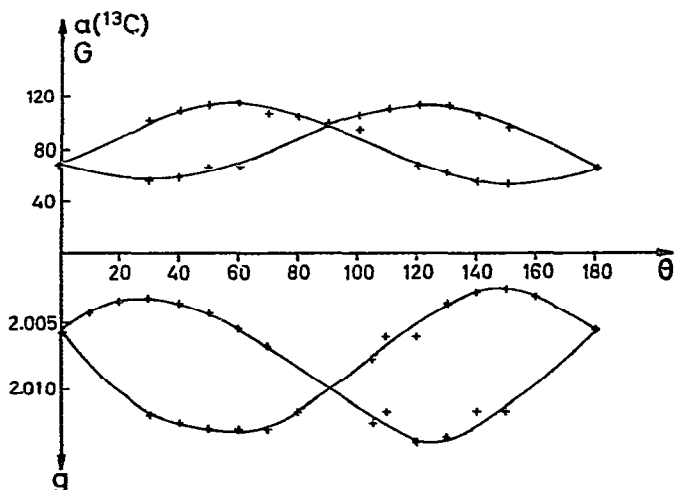
Fig. 2. Angular variation of the ^{13}C hyperfine splitting and the g-factor for $\cdot CHCl_2$ in single crystal CH_2Cl_2. The magnetic field has the direction $(\cos\theta, \sin\theta, 0)$.
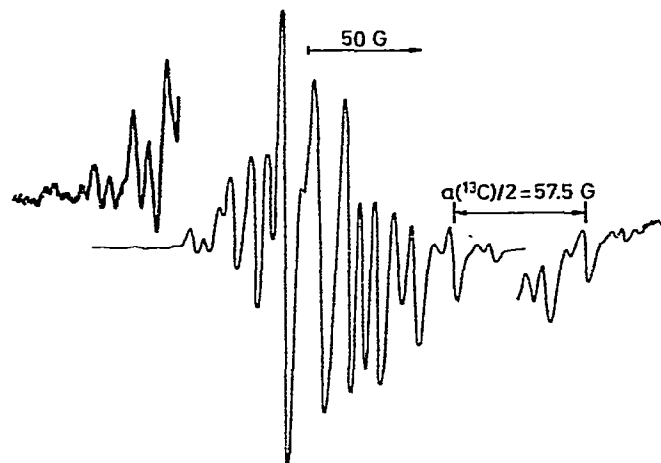
Fig. 3. Single crystal spectrum of $\cdot CHCl_2$ in single CH_2Cl_2. The magnetic field has the direction $(\cos 60, \sin 60, 0)$. ^{13}C hyperfin lines on the wings are shown with an increased gain of 200.

$= 114$ G and is also considered to be nonplanar [7]. One would expect that $a(\cdot CH_2Cl) < a(\cdot CHCl_2) < a(\cdot CCl_3)$ in agreement with the finding for the corresponding fluororadicals [8], but there is no experimental data for the $\cdot CH_2Cl$ radical to confirm this hypothesis. The spectrum of fig. 3 remains essentially the same at temperatures between 14 and 133 K. The ^{13}C splitting at 133 K is equal to the splitting at 77 K.

4. Discussion

Previous investigators [1–3] have concluded that monochloro and dichloro organic radicals are planar or nearly planar. This conclusion is based on an analysis of ESR data of the anisotropic ^1H and ^{35}Cl hyperfine couplings. Thus, in $\cdot CH_2Cl$ the angle α between the CH_2 plane and the C–Cl bond was estimated to be $\alpha = 7°$. This result was obtained by adjustment of α to obtain the best fit between experimental and calculated line positions of single crystal spectra. A line shape analysis of single crystal spectra of $\cdot CHCl_2$ was recently performed [5] to confirm the planar structure previously deduced from ESR and ELDOR spectroscopy [3].

Thus, the radicals would have the structure shown in fig. 1, with $\alpha \approx 0$. This conclusion must be modified to conform with the ^{13}C data obtained here. The model we propose is one of rapid inversion through $\alpha = 0$. This will result in an increase in the ^{13}C splitting compared to a planar geometry, but will not affect the ^1H

or ^{35}Cl hyperfine couplings significantly. These statements will now be justified.

The dipolar hyperfine couplings of ^{13}C, ^{1}H and ^{35}Cl and the quadrupole couplings of ^{35}Cl are not very sensitive to a change from a planar to a pyramidal geometry. This has been verified theoretically [5] for the $\cdot$CHCl$_2$ radical for the geometries with $\alpha = 0°$ and $\alpha = 30°$. The effect on the isotropic couplings is quite small for $a(^{35}$Cl) and $a(^1$H) according to the diagrams in fig. 4 of ref. [5]. The effect on $a(^{13}$C) is large. The experimental value of $a(^{13}$C) is consistent with a nonplanar structure ($\alpha \approx 25°$) or a rapidly inverting radical.

We cannot distinguish between a nonplanar structure and a rapidly inverting radical from the magnitudes of the coupling constants. These two cases can be distinguished experimentally by determining the directions of the principal axes of the coupling tensors. For the planar ($\alpha = 0°$) $\cdot$CHCl$_2$ radical all the coupling tensors will have a common principal axis perpendicular to the radical plane. The other "in-plane" components of the coupling tensors are along and perpendicular to the corresponding C—H and C—Cl bonds. For the nonplanar ($\alpha = 30°$) $\cdot$CHCl$_2$ radical there is no common principal axis. On the basis of available theoretical data *, one can in fact estimate that the maximum coupling of the two chlorines occurs at orientations which differ by about 20°. A similar deviation occurs for the corresponding components of the other coupling tensors. A deviation of this magnitude should be observable in the single crystal spectra. One notes for instance that a deviation of 7° was deduced from single crystal spectra of the $\cdot$CH$_2$Cl radical [1]. A value of 7° is probably comparable to the uncertainty in the determination of the relative orientations, however. Within this estimated uncertainty the experimental data obtained here and the simulations reported previously are consistent with the assumption of a common principal axis for the g-tensor, the ^{13}C, ^{1}H and ^{35}Cl hyperfine couplings. It is proposed that the spectrum shown in fig. 3 in fact corresponds to a field orientation which is perpendicular to the plane of one of the two sites. This is supported by the fact that the g-value, $g = 2.0025$, is close to the free electron value, $g_e = 2.0023$, for this particular orientation. The nonplanar $\cdot$CCl$_3$ radical has $g > g_e$ [9].

These observations show that the $\cdot$CHCl$_2$ radical must be nearly planar at least on the time scale of an ESR measurement. We have already noted that the val-

ue of $a(^{13}$C) is inconsistent with the assumption of a rigid-planar structure. It is concluded that the $\cdot$CHCl$_2$ radical in a crystalline CH$_2$Cl$_2$ matrix at 77 K converts rapidly between two equivalent pyramidal structures. We now summarize some theoretical data to support this conclusion.

Ab initio Hartree—Fock calculations [5] have indicated that the equilibrium geometry of $\cdot$CHCl$_2$ corresponds to an angle $\alpha = \pm 30°$ between the C—H bond and the plane Cl—C—Cl. The potential barrier at $\alpha = 0°$ is very shallow, however, permitting rapid inversion to occur. The calculated height of the barrier is in fact comparable to the infrared transition energies of $\cdot$CHCl$_2$ observed in an argon matrix [10] of about 1000 cm^{-1}. Thus, inversion would occur at a rate comparable to an infrared frequency of about 3×10^{13} Hz. This frequency is too high to permit observation of the two interconverting pyramidal structures. The Hartree—Fock calculations predict for instance a difference of the ^{13}C coupling for $\alpha = 0°$ and $\alpha = 30°$ of the order $\Delta\omega = 140$ MHz. From this value one finds that in the fast motional limit, $\tau\Delta\omega \ll 1, \tau \ll 1/(2\pi \times 140 \times 10^6) = 1.2 \times 10^{-9}$ s. The fact that the spectrum of fig. 3 remains the same between 14 and 133 K indicates that inversion takes place even at the lowest attainable temperature. Thus, by ESR spectroscopy one sees a planar radical provided that the frequency of the interconversion is significantly higher than $\tau^{-1} = 10^9$ Hz. The main effect of inversion is that $a(^{13}$C) is larger than in a rigid planar $\cdot$CHCl$_2$ radical. Calculations on $\cdot$CCl$_3$ indicate a similar low barrier to inversion. Thus, one might suspect a similar behaviour in this case, but here the ^{13}C data are missing.

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* Auxiliary results of the ab initio calculations reported in ref. [5].