

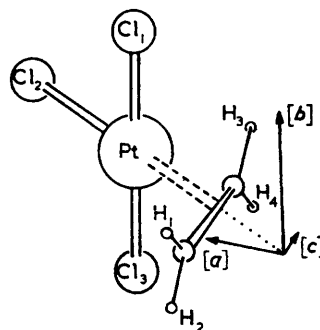
938. A Proton Magnetic Resonance Study of Zeise's Salt.

By S. MARIČIĆ, C. R. REDPATH, and J. A. S. SMITH.

Proton magnetic resonance spectra have been recorded for single crystals of $K[PtCl_3C_2H_4] \cdot D_2O$ about three axes at various orientations with respect to the applied magnetic field. A single crystal of the ordinary hydrate, $K[PtCl_3C_2H_4] \cdot H_2O$, and polycrystalline samples of the anhydrous material, have also been studied. The results are consistent with a planar configuration of the hydrogen atoms of the C_2H_4 molecule oriented at right angles to the planar- $PtCl_3$ unit, with the interproton vector of each CH_2 group parallel to the b -axis of the crystal and the $Cl-Pt-Cl$ line. The C_2H_4 molecule appears to be undergoing large-amplitude rotational oscillations about at least two axes, namely, the carbon-carbon bond and the perpendicular to the molecular plane. For this reason, an accurate estimate of the interhydrogen distances in the molecule cannot be made, although it seems to be little distorted from its ground-state configuration in the gas.

ALTHOUGH the stereochemistry of ethylene as a ligand in Zeise's salt,¹ potassium trichloro(ethylene)platinate(II) monohydrate, $K[PtCl_3C_2H_4] \cdot H_2O$, is generally regarded as settled, no detailed structural investigation of this compound has been reported. The resonance theory² and the π -complex theory³ lead essentially to similar configurations (Fig. 1) in

FIG. 1. Stereochemistry of the $[PtCl_3C_2H_4]^-$ ion (position of origin arbitrary).



that the hydrogen atoms of the ligand and the $PtCl_3$ group in $[PtCl_3C_2H_4]^-$ should lie in perpendicular planes so disposed that the line from the platinum atoms which bisects the carbon-carbon bond is perpendicular to the plane of the hydrogen atoms (which is parallel to, but not necessarily coincident with, the carbon-carbon bond).

In various X -ray structure determinations of olefin complexes,^{4,5} the hydrogen atoms have not been resolved, but the general correctness of this configuration has been checked by resolution of the carbon atoms, or by the position of a substituent. The two X -ray studies^{6,7} of Zeise's salt are more approximate. Reasonably consistent co-ordinates are quoted for the platinum and chlorine atoms; they lie in a plane which makes an angle of $23 \cdot 2^\circ$ ⁶ or $23 \cdot 6^\circ$ ⁷ with $[a]$ and has the $Cl_1-Pt-Cl_3$ line parallel to $[b]$ (Fig. 1). In Bokii and Kukina's study,⁷ the carbon atoms are resolved and a bond length of $\sim 1 \cdot 5 \text{ \AA}$ is found; however, the bond is not perpendicular to the $PtCl_3$ plane and appears to be off-centre (estimated standard deviations for the co-ordinates are not given).

¹ Zeise, *Pogg. Ann.*, 1827, **9**, 632.

² Winstein and Lucas, *J. Amer. Chem. Soc.*, 1938, **60**, 84; Douglas, *ibid.*, 1953, **75**, 4839.

³ Dewar, *Bull. Soc. chim. France*, 1951, **18**, C71, C79; Chatt and Duncanson, *J.*, 1953, 2939.

⁴ Holden and Baenziger, *J. Amer. Chem. Soc.*, 1955, **77**, 4987; Dempsey and Baenziger, *ibid.*, p. 4984; Luxmore and Truter, *Acta Cryst.*, 1962, **15**, 1117.

⁵ Alderman, Owston, and Rowe, *Acta Cryst.*, 1960, **13**, 150.

⁶ Wunderlich and Mellor, *Acta Cryst.*, 1954, **7**, 130; 1955, **8**, 57.

⁷ Bokii and Kukina, *Kristallografiya*, 1957, **2**, 3.

The high-resolution proton magnetic resonance spectrum⁸ of the $[\text{PtCl}_3\text{C}_2\text{H}_4]^-$ ion in deuterium oxide shows a strong singlet attributed to the ethylenic protons with weak sidebands, 34 c./sec. apart, produced by spin-spin coupling to ^{195}Pt ; in a saturated solution in deuterium oxide with a little hydrogen chloride, the singlet is 176 c./sec. to the low-field side of cyclohexane as external reference at 40 Mc./sec. and is in the usual position for olefin hydrogen.⁹ These results are in agreement with a symmetrically co-ordinated ethylene molecule. Infrared arguments^{10,11} indicate symmetrical co-ordination, but differ in the interpretation of the structure and in the degree of distortion proposed for the C_2H_4 group.

We have attempted to confirm the configuration given in Fig. 1 by a study of the broad-line proton magnetic resonance (p.m.r.) spectrum of single crystals of the deuterate, $\text{K}[\text{PtCl}_3\text{C}_2\text{H}_4]\cdot\text{D}_2\text{O}$. In previous p.m.r. studies of dehydrated Zeise's salt¹² and $[\text{PtCl}_2\text{C}_2\text{H}_4]_2$,¹³ polycrystalline samples were used. The results were consistent with the π -complex structure, although in $[\text{PtCl}_2\text{C}_2\text{H}_4]_2$ the ethylene molecule appeared to have a configuration intermediate between those of gaseous ethylene and ethane in an eclipsed configuration with two of the *cis*-protons removed.

EXPERIMENTAL

Two samples of $\text{K}[\text{PtCl}_3\text{C}_2\text{H}_4]\cdot\text{H}_2\text{O}$ were used. The first was dehydrated directly *in vacuo* over sulphuric acid, the process being followed by the change in weight. Although the loss of water was apparently quantitative, and this sample was used for p.m.r. measurements, traces of water remained and were detected in the infrared spectrum as peaks at 500 and 1613 cm^{-1} . Dehydration of large crystals produces a collapse of the crystal lattice, so that it is clearly necessary to grow the crystals from deuterium oxide. The dehydrated sample (2.2 g.) was dissolved in deuterium oxide (15 ml.) containing 6% of deuterium chloride,¹⁴ in a jacketed cell whose temperature was maintained at 37° by circulation of water from a thermostat-bath. Overnight cooling to 20° gave fine needle-like crystals; one such crystal, 4 mm. long with well-developed faces, was selected and the needle-axis identified as $[c]$ by X-ray methods. We use here Wunderlich and Mellor's values⁶ of $a = 10.70$, $b = 8.42$, and $c = 4.81$ Å, with $\beta = 97^\circ$; the space group is $P2_1$ and there are two molecules in the unit cell. The crystal was mounted with "Araldite" adhesive on a stirrer shaft with $[c]$ vertical and immersed in the solution saturated at 37° with freshly dehydrated material. The temperature of the thermostat-bath was lowered by manual adjustment of the mercury contact of the toluene regulator; as soon as the crystal showed signs of growing, an automatic control was switched on and the mercury contact gradually lowered, so that the temperature dropped by about 1.2° every 24 hr. The crystal was simultaneously rotated, the direction of rotation being reversed every 5 min. After 10 days, the crystal was elongated along an axis perpendicular to $[c]$, later identified as $[b]$. It was remounted about this axis and regrown from solution, after addition of fresh dehydrated material to maintain saturation. Three such processes gave a crystal of weight 1.2 g., approximately $15 \times 9 \times 5$ mm. Small secondary growths that developed during cooling were removed by a fine jet of aluminium oxide in a special abrasive unit.¹⁵

Goniometric examination of the crystal showed well-developed faces belonging to $\{102\}$, $\{100\}$, and $\{120\}$; the positions of $[b]$ and $[c]$ were also checked by back-reflection X-ray photographs. Proton magnetic resonance spectra were recorded about three axes; the first two, axes I and II, corresponded to the crystallographic axes $[b]$ and $[c]$. Axis III was a non-crystallographic axis perpendicular to the plane of the ethylene molecule; for a symmetrical ion, axis III is therefore parallel to the Pt-Cl₂ bond in Fig. 1, which in Wunderlich and Mellor's

⁸ Powell and Sheppard, *J.*, 1960, 2519.

⁹ Smith, unpublished work. We are grateful to Dr. H. J. Bernstein of the National Research Council, Ottawa, for obtaining these spectra.

¹⁰ Babushkin, Gribor, and Hel'man, *Doklady Akad. Nauk S.S.S.R.*, 1958, **123**, 461.

¹¹ Powell and Sheppard, *Spectrochim. Acta*, 1958, **13**, 69.

¹² Maričić, Thesis, Zagreb, 1959.

¹³ Reeves, *Canad. J. Chem.*, 1960, **38**, 736.

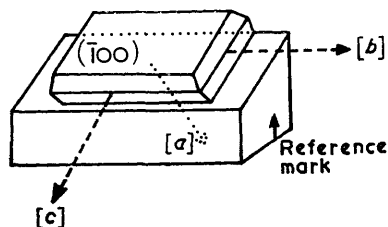
¹⁴ Brown and Groot, *J. Amer. Chem. Soc.*, 1942, **64**, 2223.

¹⁵ Pringle, *Proc. Leeds Phil. Lit. Soc. (Sci. Sect.)*, 1960, **8**, 177.

structure is inclined at $16^{\circ} 12'$ to (100) and $23^{\circ} 12'$ to $[a]$ in a right-handed co-ordinate system. The crystal was therefore cemented with (100) lying on the upper surface of a specially machined polytetrafluoroethylene platform so that (100) was $16^{\circ} (\pm 1^{\circ})$ away from the horizontal, $[c]$ sloped down the wedge, and $[b]$ was parallel to its long edge (Fig. 2). For a second check, the crystal and wedge were placed on a "Unicam" X-ray camera and the wedge was rotated through 23° in an anticlockwise direction, viewed along $[b]$; $[a]$ is then vertical and a back-reflection X-ray photograph gave horizontal layer lines. A radiofrequency coil was then built around the crystal and the orientation in the magnetic field checked as described in a previous paper.¹⁶

During these operations with the deuterated single crystal, precautions were always taken to exclude moisture. During the X-ray work, the crystal was enclosed in a thin Polythene bag, and during the p.m.r. work it was sealed into the coil-former with "Kel-F" wax. Despite these precautions, some exchange of deuterium for hydrogen occurred and an analysis was

FIG. 2. Crystal mounting for the axis III measurements.



necessary. A fragment (0.3 g.) of the crystal was powdered and pumped in a specially-dried vacuum line to remove the deuterium oxide; an infrared analysis of this sample * gave a molecular ratio $D_2O : HOD$ of 2.59 to 1. The residue was treated with anhydrous pyridine, the ethylene was freed from pyridine vapour in a solid carbon dioxide trap, and its composition determined in a mass spectrometer.† The molecular ratio $C_2H_4 : C_2H_3D$ was 3.50 : 1. The required corrections to the second-moment data are discussed below. Previous experience¹¹ with deuterated samples indicated no exchange of ethylene with the excess of deuterium oxide in 3 months; our analysis was made 18 months after the crystal was grown, by which time it had acquired a thin surface layer of finely divided platinum, which may have catalysed the exchange.

A second sample was also prepared in this laboratory¹⁷ and used to grow a large crystal ($10 \times 7 \times 4$ mm.) of $K[PtCl_3C_2H_4] \cdot H_2O$ and a smaller crystal of the deuterated salt for some preliminary experiments. The crystal of the hydrate was examined goniometrically, and the faces were identified and used to mount the crystal about $[b]$. The specimen was then set in the field as described previously.¹⁶ A smaller deuterated crystal was also examined on a goniometer and set with $[b]$ parallel to the axis of rotation. No chemical analysis was made of these two crystals.

The p.m.r. spectra were recorded at 16.435 Mc./sec. in a radiofrequency-bridge apparatus, described previously.¹⁸ The line-widths ($\Delta H_{m.sl.}$) were read directly off the recorded spectra by means of a specially calibrated transparent scale which allowed for a small non-linearity of the magnetic-field sweep. The second moments ($\langle \Delta H^2 \rangle$) were calculated on a Ferranti "Pegasus" computer with a programme written in "autocode"; ordinates read off the derivative curve were fed into the machine, which also applied a time-constant correction before calculating the second moment. The mean estimated standard deviation of $\Delta H_{m.sl.}$ is 0.3 gauss and of $\langle \Delta H^2 \rangle$ 1.6 gauss².

RESULTS

The first problem was to determine the temperature at which to record the spectra. The second moments of the dehydrated powder $K[PtCl_3C_2H_4]$ and $[PtCl_2C_2H_4]_2$ are compared in

* We are grateful to Mr. G. F. Aitchison, A.E.R.E. (Harwell), for this analysis.

† The mass spectrometric work was provided by Dr. R. A. Saunders of Imperial Chemical Industries Limited, Dyestuffs Division.

¹⁶ Emsley and Smith, *Trans. Faraday Soc.*, 1961, **57**, 893.

¹⁷ Chatt and Searle, *Inorg. Synth.*, 1957, **5**, 220; McNevin, Giddings, and Foris, *Chem. and Ind.*, 1958, 557.

¹⁸ Smith, *Discuss. Faraday Soc.*, 1955, **19**, 207.

Second moments (gauss²) for two ethylene complexes.

	77°K	300°K	Authors
K[PtCl ₃ C ₂ H ₄]	15.0 ± 1.7	13.1 ± 1.3	This paper
[PtCl ₂ C ₂ H ₄] ₂	13.7 ± 1.0	10.6 ± 1.0	Reeves ¹³

the Table. The two second moment values for K[PtCl₃C₂H₄] are not significantly different, but in view of Reeves's results it is possible that there is a small increase at low temperatures. This point will be taken up in the Discussion. A single crystal of K[PtCl₃C₂H₄]D₂O mounted about [b] and with $H_0[a] = 56^\circ$, was also studied at 145° and 300°K; the line widths were 13.5 ± 0.8 and 12.4 ± 0.3 , respectively. Again, the difference is not significant, although in the same direction as for the powder. Unfortunately T_1 (the spin-lattice relaxation time) rose on cooling and the signal-to-noise ratio deteriorated considerably. Because of this, we decided to study the spectra at room temperature.

Some preliminary studies were made on the hydrate K[PtCl₃C₂H₄].H₂O mounted about [b] in order to estimate the effects of the water molecule on the spectrum. In Fig. 3 we plot the angular variation of the second moment derived graphically; no absolute measurements of angle were made and the scale of θ has been fixed by setting $\theta = 90^\circ$ at the first maximum. For this mounting, the principal interproton vector of the ethylene molecule, H_1-H_2 , should

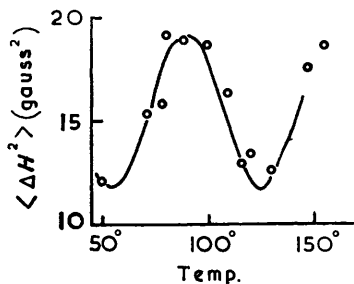


FIG. 3. Angular variation of $\langle \Delta H^2 \rangle$ for K[PtCl₃C₂H₄].H₂O about [b].

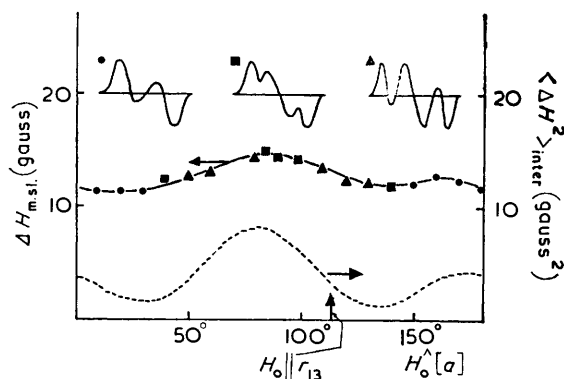


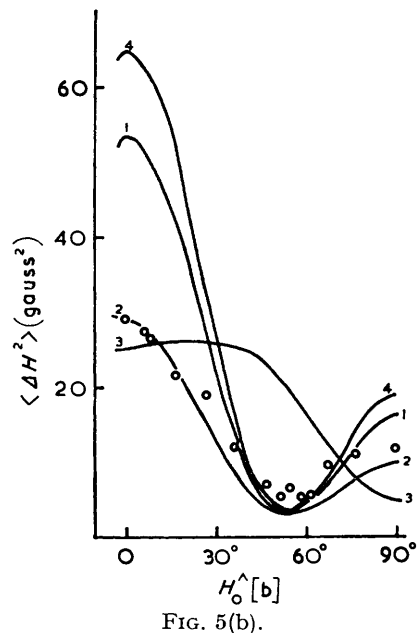
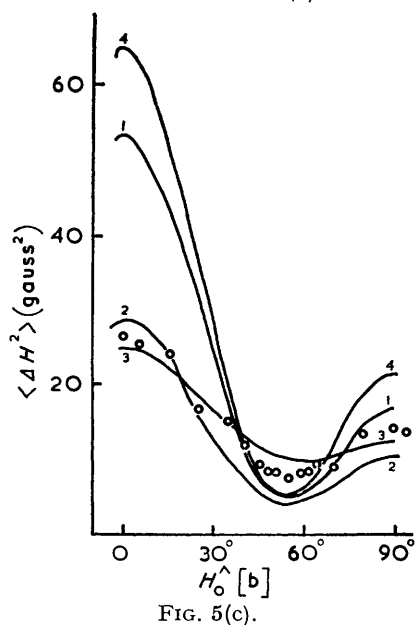
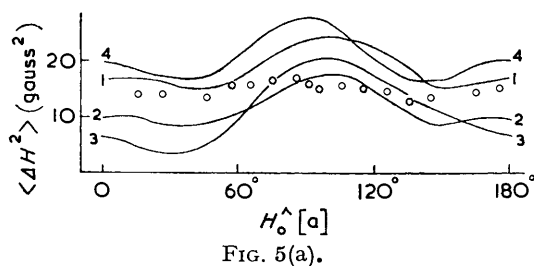
FIG. 4. Line widths ($\Delta H_{m.sl.}$) and approximate line shapes for K[PtCl₃C₂H₄].D₂O about [b]. The broken line is the calculated intermolecular second moment.

remain always perpendicular to the magnetic field, and the main variation in $\langle \Delta H^2 \rangle$ should be due to the cross-terms H_1-H_3 and H_1-H_4 . Despite the limited range of angle covered and the poor signal-to-noise ratio, it is clear from the results that the water molecule has an overwhelming effect on the spectrum, so that a deuterated crystal is necessary.

The smaller deuterated crystal gave more encouraging results. Although the signal-to-noise ratio was too poor to enable reliable second moments to be calculated, the line width $\Delta H_{m.sl.}$ changed very little on rotation of the crystal in the magnetic field about [b] [no absolute measurement of the orientation of H_0 in (010) was made], and the average value over 180° was 12.2 gauss. The larger deuterated crystal gave considerably stronger signals about [b] and a complete investigation was made. Fig. 4 gives values of $\Delta H_{m.sl.}$ for the outer peaks of the derivative curve at various values of the angle $H_0 \parallel [a]$. The average value over 180° was 12.8 gauss. The Figure also gives some indication of the sequence of line shapes observed, which is generally similar to that of the smaller crystal. Fig. 5(a) gives the angular variation of $\langle \Delta H^2 \rangle$ about axis I ([b]) with respect to the angle $H_0 \parallel [a]$, and Figs. 5(b and c) the angular variation of $\langle \Delta H^2 \rangle$ for axis II ([c]) and axis III (parallel to Pt-Cl₂) with respect to the angle $H_0 \parallel [b]$. All second-moment measurements have been corrected for the effect of modulation amplitude.¹⁹ A further factor is required to allow for isotopic exchange. The molecular ratio 1:2.6 of HOD:D₂O was neglected, since the intramolecular second moment of HOD itself in

¹⁹ Andrew, *Phys. Rev.*, 1953, **91**, 425.

the powder should be only 0.3 gauss² and its intermolecular contribution should also be small. However the intramolecular second moment of C₂H₃D is half that of C₂H₄ (if the H-D terms are neglected), so that we require a correction factor of $2m + 2/m + 2$, where C₂H₃D : C₂H₄ is $m : 1$, and we assume that the intermolecular terms are reduced in the same ratio. This factor is included in the second moments plotted in Figs. 5(a-c), and m has been calculated with the assumption that its initial value was zero and that it increased linearly with time to a final value of 0.286 over the period of the experiments. These corrections are small; the maximum effect on the axis III measurements is about 10%. This was checked by remounting



FIGS. 5(a), (b), and (c). Angular variation of $\langle \Delta H^2 \rangle$ for $K[PtCl_3C_2H_4] \cdot D_2O$ (o) compared with four calculated sets of values, (a) about axis I, (b) about axis II, and (c) about axis III. The numbers refer to the "case" numbers in the text.

the crystal about axis I after the axis II measurements and recording spectra at five different orientations in the applied magnetic field. The line shapes were very similar to the corresponding spectra taken three months before and the line widths were identical within experimental error.

DISCUSSION

For the single crystal of $K[PtCl_3C_2H_4] \cdot H_2O$, no absolute measurements of angle were made, so that the complete orientation of the water molecule cannot be derived. However, some general conclusions may be drawn from Fig. 3. Since both water molecules in the unit cell are related by a 2_1 axis, their second-moment contributions along a given direction perpendicular to $[b]$ will be the same. The angular variation of the total second moment should therefore show a $[3 \cos^2 \delta \cos^2(\phi - \phi_0) - 1]^2$ dependence, where $\phi - \phi_0$ is the angle between H_0 and the projection of the interproton vector of the water molecule on (010) and δ this angle of projection; we assume that the ethylene second moment and the intermolecular terms are independent of $\phi - \phi_0$ and that the water molecules are not rotating.

The angular variation shown in Fig. 3 is then explained if δ is approximately 0° , *i.e.*, the interproton vector lies parallel, or nearly parallel, to (010). The maximum then corresponds to $|\phi - \phi_0| = 90^\circ$, with minima at $\pm 35^\circ$ on either side, *i.e.*, at $|\phi - \phi_0| = 55^\circ$ or 125° . The larger maximum at $|\phi - \phi_0| = 0^\circ$ or 180° was not recorded. With these assumptions, a least-squares fit to the experimental points (continuous curve) gave an interproton distance in the water molecule of $1.65 \pm 0.06 \text{ \AA}$, in reasonable agreement with values for other hydrates.²⁰ No corrections for thermal oscillations have been applied to this value, but they are unlikely to increase the large error of 0.06 by more than 0.02 \AA . Non-zero but small values of δ are not excluded; for example, if we place the minimum at $(\phi - \phi_0) = 50^\circ$ and 130° , we deduce a value of δ of 26° . We may say that the interproton vector of the water molecule is parallel to (010) within $\pm 30^\circ$. The oxygen atom of the water molecule has been located in one of the X-ray structure analyses,⁷ and is found to have O-Cl distances to chlorine atoms in different neighbouring $[\text{PtCl}_3\text{C}_2\text{H}_4]^-$ ions of 2.9 and 3.3 \AA , which are comparable with hydrogen-bonded O-Cl distances of 2.99 and 3.15 \AA recorded elsewhere.²¹ We may then locate the hydrogen atoms approximately along these O-Cl contacts; if the O-H...Cl bond were exactly linear, the H₂O plane would be inclined at 29° to (010), which is consistent with the second-moment data.

We consider next the results for $\text{K}[\text{PtCl}_3\text{C}_2\text{H}_4] \cdot \text{D}_2\text{O}$ and first the angular variation of the second moment. For rotation about $[b]$ [Fig. 5(a)], the changes are small and indicate that the second moment is predominantly determined by a vector H₁-H₂ which makes a constant angle with the applied field, as expected from Fig. 1. About axes II and III [Figs. 5(b and c)], the angular variation is much more marked and, further, the maximum occurs when $[b]$ is parallel to H₀, indicating that H₁-H₂ is parallel, or nearly so, to this axis. This parallelism is not required by the $P2_1$ symmetry and, from the fact that the Cl₁-Pt-Cl₃ line is also parallel to $[b]$ in both X-ray structure analyses, we have strong evidence for the correctness of a symmetrical π -complex structure.

Unfortunately, we have been unable to find a satisfactory "rigid-lattice" model which predicts correctly the measured second moments and the observed line shapes. The four continuous curves in Figs. 5(a-c) summarise calculations performed by a Ferranti "Pegasus" computer for five different configurations of a co-ordinated ethylene molecule.

(1) C₂H₄ has the same dimensions as in the gas,²² namely, H₁-H₂ = 1.840 and H₁-H₃ = 2.484 \AA .

(2) The HCH angle is opened out to give H₁-H₂ = 2.10 and the C=C bond stretched so that H₁-H₃ = 2.50 \AA . The molecule remains planar.

(3) H₁-H₂ and H₃-H₄ remain unchanged in length, but both are twisted by 30° in opposite directions about C=C. This configuration bears some similarity to the shape of the first excited state of ethylene.²³

(4) This configuration is derived from ethane in an eclipsed conformation by removal of a pair of *cis*-hydrogen atoms and some change in the bond distances, *i.e.*, H₁-H₂ = 1.772 and HCH = 109° . A similar structure has been used to explain second-moment measurements on polycrystalline $[\text{PtCl}_2\text{C}_2\text{H}_4]_2$,¹³ and the kind of distortion involved has been predicted by several authors.

(5) As in (4), but a pair of *trans*-hydrogen atoms is removed from an ethane molecule in a staggered conformation; the bond distances are the same as in (4). The calculated values are not plotted separately, since they appear to be almost identical with those of case (4).

It is clear that none of these configurations gives a good fit to the experimental results;

²⁰ McGrath and Silvidi, *J. Chem. Phys.*, 1961, **34**, 322.

²¹ Nakamoto, Margoshes, and Rundle, *J. Amer. Chem. Soc.*, 1955, **77**, 6480.

²² Bartell and Bonham, *J. Chem. Phys.*, 1957, **27**, 1414.

²³ Walsh, *J.*, 1953, 2325.

the planar models follow the expected angular variation but generally give too large second moments, except in case (2) which is improbable structurally.

Further difficulties arise with calculations of line shape about $[b]$. The observed spectra are unfortunately rather unsymmetrical (Fig. 6), but the main problems come

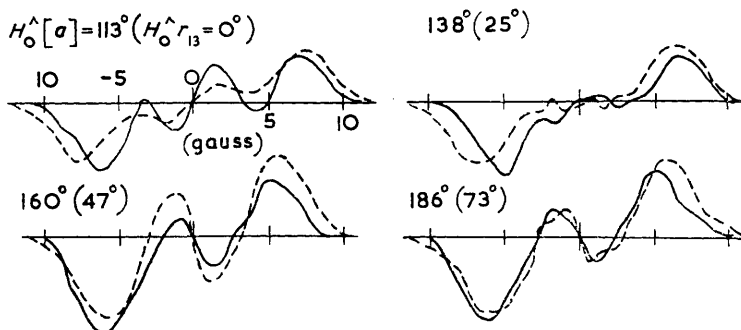


FIG. 6. Observed (—) and calculated (---) line shapes about $[b]$ ($r_{12} = 1.84$, $r_{13} = 2.48 \text{ \AA}$; $\beta^2 = 5 \text{ gauss}^2$).

from the unexpectedly large intermolecular terms—at certain orientations they become so important as to influence decisively the line shape. The most important variations about $[b]$ are expected to occur for the term A_{13} (and A_{24}), defined as²⁴

$$A_{ij} = (3 \cos^2 \theta_{ij} - 1)/r_{ij}^3$$

in which r_{ij} is the distance between the i 'th and j 'th proton and $\cos \theta_{ij}$ is the angle between this vector and the applied magnetic field. The calculations were made for a four-spin system, by assuming $A_{12}, A_{34} \gg A_{13}, A_{24}$, with $r_{12} = 1.84 \text{ \AA}$ and $r_{13} = 2.48 \text{ \AA}$, and an average value of β^2 (intermolecular broadening) of 5 gauss^2 . In Fig. 5, H_0 is parallel to r_{13} at $H_0^{\hat{a}} = 113^\circ$, so at this point $(3 \cos^2 \theta_{13} - 1)$ has its maximum value of 2; the observed sequence of line shapes is then reproduced reasonably well by the calculations for values of $H_0^{\hat{a}}$ above 113° (to 196°) but not below this value (Fig. 6). The explanation of the latter effect is fairly certainly the large rise in the intermolecular terms below 113° (see Fig. 4), which invalidates the four-spin approximation, in particular by the close approach to H_1 of a hydrogen (H_3') in another molecule related to the first by a z -axis displacement. Similar effects complicate the line shapes about the other axes. Above $H_0^{\hat{a}} = 113^\circ$, the intermolecular terms are small, A_{13} and A_{24} drop considerably, and between 149° and 189° the curves look "two-spin" in character, but the calculated splittings of the absorption line are about 20% smaller than the experimental.

The results suggest that the p.m.r. spectra are being "narrowed" by some form of molecular motion. Reduction of the second moment by rotation is improbable. First, rotation of the ion as a whole is excluded by the X -ray evidence. As for the C_2H_4 molecule, if we take as our axes the moment of inertia axes A , B , and C (with $I_A < I_B < I_C$), rotation about axes B and C is excluded by X -ray structure analyses in which the carbon atoms have been resolved,⁵ and about axis A by the p.m.r. second moments, which would be considerably smaller if this were occurring. All previously recorded infrared frequencies would have too small an effect. We therefore turn to the case of rotational oscillation; Reeves¹³ has mentioned this possibility but gives no calculations. Consider a C_2H_4 molecule, of the same dimensions as in the gas, undergoing rotational oscillation about its three axes A , B , and C . The effect of each mode is to average $\cos^2 \theta$ according to the equation

$$\langle \cos^2 \theta \rangle = \cos^2 \theta_0 - \frac{1}{2} \alpha^2 \sin^2 \theta' \cos 2\delta, \quad (1)$$

²⁴ Itoh, Kusaka, Yamagata, Kiriya, and Ibamoto, *J. Phys. Soc. Japan*, 1953, **8**, 293.

in which θ_0 represents the angle between the interproton vector and the field H_0 in the absence of motion, α the angular amplitude, θ' the angle between the axis of oscillation and H_0 , and $\delta = \phi - \phi_0$ is the azimuthal angle in a plane perpendicular to the axis of oscillation with respect to an azimuth defined by the intersection of this plane and another containing both the axis of oscillation and H_0 . These quantities are illustrated in Fig. 7,

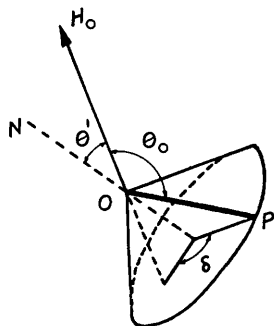


FIG. 7. Definitions of the terms in eqn. (1).

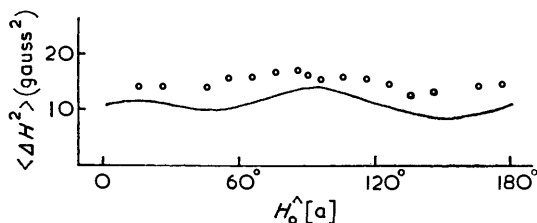


FIG. 8(a).

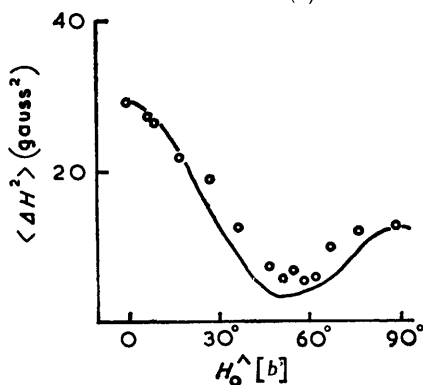


FIG. 8(b).

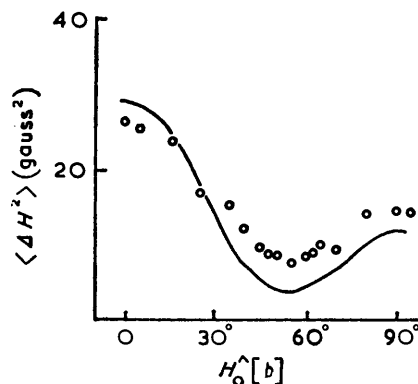


FIG. 8(c).

Figs. 8(a), (b), and (c). Experimental values of $\langle \Delta H^2 \rangle$ (O) compared with calculated values for an ethylene molecule with oscillational amplitudes of $\alpha(A) = 29^\circ$ and $\alpha(C) = 19^\circ$; (a) about axis I, (b) about axis II, and (c) about axis III.

in which OP is any interproton vector, H_0 the field direction, and ON the axis of oscillation. The formula is adapted from one proved by Andrew²⁵ for the case of simple harmonic motion; α is assumed to be small, but errors in $\langle \cos^2 \theta \rangle$ will be less than 1% even when $\alpha = 20^\circ$. We then assume that the C_2H_4 molecule is undergoing rotational oscillation about axis A with an amplitude $\alpha(A)$ (not distinguishable here from a torsional oscillation of the same amplitude) and about axis C with an amplitude $\alpha(C)$; the molecule almost certainly has a comparable oscillation about axis B , but since this does affect the principal interproton vectors H_1-H_2 and H_3-H_4 , it will be a secondary correction to the p.m.r. data and we can derive little reliable information as to its magnitude. We next assume that the correction terms can be added, *i.e.*, equation (1) becomes:

$$\langle \cos^2 \theta \rangle = \cos^2 \theta_0 - \frac{1}{2} \alpha^2(A) \sin^2 \theta_A' \cos 2\delta_A - \frac{1}{2} \alpha^2(C) \sin^2 \theta_C' \cos 2\delta_C. \quad (2)$$

²⁵ Andrew, *J. Chem. Phys.*, 1950, **18**, 615.

Equation (2) is then applied to the principal interproton vectors, namely, H_1-H_2 , H_3-H_4 , H_1-H_3 , and H_2-H_4 ; the intermolecular term is reduced by a factor of 0.72, obtained by dividing the experimental second moment at 300°K by the "rigid"-lattice value. Unfortunately a range of values of $\alpha(A)$ and $\alpha(C)$ would almost certainly give a reasonable fit to the experimental second moments; as one example, if we assume $\alpha(A) > \alpha(C)$, and take $\alpha(A) = 0.50$ rad. = 29° and $\alpha(C) = 0.33$ rad. = 19°, the continuous curves given in Figs. 8(a), (b), and (c) are derived.

Nevertheless, oscillational amplitudes of this order are unusual in molecules, and it is interesting that there is possibly some further evidence. The first¹³ is the temperature-dependence of the second moments of $K[PtCl_3C_2H_4]$ and $[PtCl_2C_2H_4]_2$ (see the Table). It is unlikely that this behaviour is due to a phase transition, at least down to 145°K, for crystals cooled to this temperature gave spectra almost identical with those obtained at room temperature except for a poorer signal-to-noise ratio, and they showed no signs of disintegration. It is therefore possibly a temperature effect associated with the reduction in oscillational amplitude with decrease in temperature. The amplitude is still considerable at 77°K, so that no calculation of interproton distances from second moments would be valid, even at that temperature, without a previous thermal correction. The second piece of evidence is the temperature factor of 8.4 found for the CH_2 group in *trans*- $[PtCl_2(C_2H_4)(NHMe_2)]$.⁵ This gives an r.m.s. amplitude $(\bar{u}^2)^{1/2}$ of 0.33 Å, and if we associate this with rocking of the C_2H_4 molecule about the Pt- C_2H_4 bond, we derive an r.m.s. amplitude of oscillation of 14°, or an angular amplitude of 20°.

The selected values of $\alpha(A)$ and $\alpha(C)$ may be related to angular frequencies $\omega(A)$ and $\omega(C)$ by the equation²⁶

$$I\omega^2\langle\alpha^2\rangle = \hbar\omega\left(\frac{1}{2} + \frac{1}{\exp\frac{\hbar\omega}{kT} - 1}\right), \quad (3)$$

in which I is the moment of inertia about the axis of oscillation. For gaseous ethylene,²² $I_A = 5.66$ and $I_C = 33.68 \times 10^{-40}$ g.cm.². We then derive $\omega(A) = 130$ and $\omega(C) = 80$ cm.⁻¹. With these values of ω , at 77°K $\alpha(A)$ is calculated as 0.30 rad. (17°) and $\alpha(C)$ as 0.18 rad. (10°). The temperature variation of α is responsible for the temperature variation of the second moment. For a co-ordinated ethylene molecule of the same dimensions as in the gas, we calculate a "rigid"-lattice value of 15.0 gauss² (inter-contribution = 3.9 gauss²); with an average of the corrections for rotational oscillation, the predicted second moment at 77°K is 13.4 gauss² and at 300° 10.8, a difference of 2.6 gauss², compared with an experimental value of 15.0 - 13.1, or 1.9 gauss². In this comparison, therefore, the variation with temperature can be explained.

The calculated values of $\alpha(A)$ and $\alpha(C)$ must be regarded as estimates only. It has been assumed that $\alpha(A) > \alpha(C)$, and the effects of all other vibrational modes apart from the rotational oscillations about A and C have been neglected. Only case (1) has been considered, and other configurations could almost certainly be made to fit the data, although Reeves's suggestion¹³ (case 4) would require oscillational amplitudes about 20% greater than those calculated by us. There is therefore no solution to the structure from the p.m.r. results which is both accurate and unique. Our main conclusions are that the ethylene molecule in Zeise's salt has the expected stereochemistry and is probably little distorted from its dimensions in the gas, but appears to be undergoing large-amplitude rotational oscillations.

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