

Nuclear Magnetic Resonance Study of Crystalline Bis(cyclooctatetraene)iron

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Received 26th June, 1972

Crystalline bis(cyclooctatetraene)iron has been studied by investigation of n.m.r. line-width and second moment variations with temperature. The experimental second moment has been compared with that calculated for the rigid lattice. It was found that, while below -185°C the rate of the motions presumably present in the crystal is not great enough to affect the second moment, above this temperature the molecules start to move at an increasing rate. At room temperature the only possible type of motion of the molecules is completely activated and consists of oscillations of the cyclooctatetraene rings. The n.m.r. data allow us to conclude that the structural disorder observed at room temperature with X-rays is of a dynamic type.

The X-ray crystal structure of bis(cyclooctatetraene)iron $(\text{C}_8\text{H}_8)_2\text{Fe}$, has been investigated, at room temperature.¹ It was found that it crystallizes in the monoclinic system; the unit cell parameters are $a = 25.13 \text{ \AA}$, $b = 10.68 \text{ \AA}$, $c = 13.98 \text{ \AA}$; $\beta = 99.6^{\circ}$. The unit cell contains 12 molecules and the space group is $C2/c$. Two crystallographically different Fe atoms were found in the unit cell; one in a general position, and the other on a twofold axis. In fig. 1 are shown the two types of molecules existing in the crystal. The molecule containing the Fe atom in a general

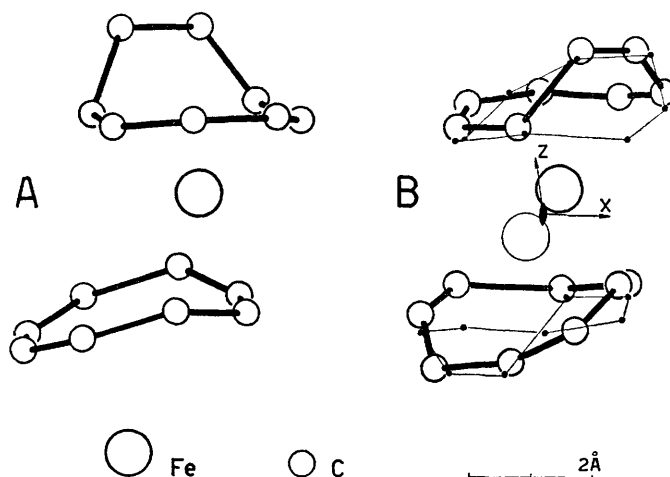


FIG. 1.—The two types of bis(cyclooctatetraene)iron molecules: A, view of the ordered molecule; B, view of the disordered molecule. Heavy and light lines show, respectively, the skeletons of the two symmetry related molecules.

position (molecule A) is ordered, while that containing the Fe atom in the twofold axis position (molecule B) is strongly affected by structural disorder and may assume two coordination modes related by the symmetry axis. Molecule B and its symmetry related pair are shown in heavy and light lines, respectively, in fig. 1. However, the differences between the two non equivalent molecules A and B are within the limits of experimental error. On the basis of X-ray data, it was not possible to state whether the structural disorder of molecule B is due to a random distribution of molecules having two alternative fixed orientations (static disorder) or to a rapid interchange of the C_8H_8 rings between the two possible coordination modes (dynamic disorder).

In the lattice there are only half as many disordered molecules as ordered ones. In each $(C_8H_8)_2Fe$ molecule in the lattice the two cyclooctatetraene rings differ in their geometrical configuration and in their mode of coordination to the central Fe atom. The central atom is π bonded to six C atoms of one ring and four of the other.

In a recent paper Allegra *et al.*² have reported some additional information on the X-ray structure of $(C_8H_8)_2Fe$ giving the fractional coordinates of the C and Fe atoms. In the same paper on the basis of the X-ray data, the possibility of the *Cc* space group is discarded and it is also reported that no basic change in the crystal structure of the compound was observed at $-100^\circ C$.

The purpose of this work is to investigate if the structural disorder, observed with X-rays, is of static or of dynamic origin and, in particular, to gain information about the motions that take place in crystalline $(C_8H_8)_2Fe$. The n.m.r. broad line technique offers a particularly useful tool for studying such problems because the line-width and the second moment of the n.m.r. spectra and their variations with temperature are very sensitive to the structural and dynamic properties of the lattice.

EXPERIMENTAL

A freshly prepared sample of $(C_8H_8)_2Fe$ was used and, to avoid decomposition, it was kept under an inert atmosphere in a sealed ampoule and stored in dry ice before the measurements. To ensure that the sample had not decomposed it was checked by electron spin resonance: the fresh sample gives no e.s.r. signal, as iron is zero-valent, while after being heated above the decomposition temperature, which is about $80^\circ C$, it gives rise to a strong e.s.r. signal due to iron ions.

All n.m.r. spectra were recorded at 16 MHz with a Varian VF-16 spectrometer, the first derivative of the proton absorption signal was recorded between $-196^\circ C$ and the decomposition temperature using a modulation-depth of one tenth of the line-width. In order to avoid saturation broadening of the absorption signals, the r.f. field was accurately maintained below the saturation value for each spectrum recorded. The inhomogeneity of the magnetic field over the sample volume was 60 mG and so was negligible compared to the observed line-width. Temperatures were measured with a copper-constantan thermocouple located on the wall of the sample tube and controlled to within $\pm 1^\circ C$ with the Varian V-4557 temperature control unit. Liquid nitrogen temperature was reached with a specially designed cryostat. E.s.r. spectra were taken with a Varian V-4502 spectrometer.

RESULTS

The behaviour of the line-width ΔH with temperature is shown in fig. 2.

At low temperature the n.m.r. line is broad; the line-width, measured between the points of maximum and minimum of the derivative of the absorption signal, at $-196^\circ C$, is $\Delta H = 12.1 \pm 0.1$ G and maintains the same value at $-185^\circ C$. Above this temperature the line begins to narrow. Narrowing is accomplished over a range of temperature of about $100^\circ C$ and is accompanied by the growth of a sharper

central line which also undergoes narrowing. The lowest temperature at which we have detected this sharper line is -139°C . However, we were able to measure the line widths of the two components separately, i.e., the broad and the sharper line, only at temperatures greater than -120°C .

The evaluation of the line-width and the relative areas of each component of the resonance signal were obtained from the best fit of the experimental line. It was found, over the whole range of temperature, that the broad component approximates to a gaussian line shape, while the narrow one approximates to a lorentzian line shape and more so as the temperature increases. The height and the width of the two lines, with the same resonance field value, were suitably chosen to obtain the best fit at each temperature. The estimated error of the line-widths obtained in this way is ± 0.1 G.

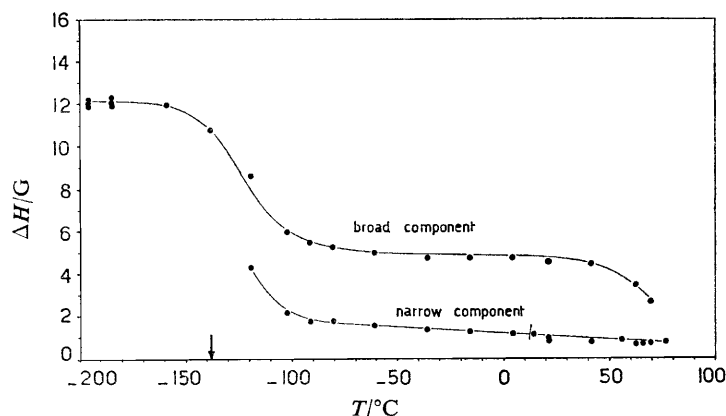


FIG. 2.—Line-width ΔH against temperature for crystalline bis(cyclooctatetraene)iron. The arrow indicates the temperature at which the narrow component appears. The solid curve was calculated with eqn (4) and (6).

The ratio of the area of the broad to that of the narrow one is about 8 at -120°C and decreases to 3.5 at 40°C . Since r.f. field intensities well below saturation for both the components were used, the ratios we have estimated are not in error due to differences in the relaxation rates.

At the end of the narrowing the broad component maintains a constant line-width of about 4.8 G over a wide range of temperature and shows a further narrowing close to decomposition temperature, whilst, over the same range of temperature, the width of the narrow component slowly decreases from 2 to about 1 G.

The values of $S^{\text{exp.}}$, the experimental second moment, were derived from the recorder tracings of the line shape derivative $f'(H)$ by means of the expression

$$S^{\text{exp.}} = \frac{\frac{1}{3} \int_0^{\infty} \frac{f'(H)(H-H_0)^3 dH}{\int_0^{\infty} f'(H)(H-H_0) dH}}{-\frac{1}{4} h_m^2} \quad (1)$$

where H_0 is the resonance field value and h_m is the amplitude of the sinusoidal field modulation.

The average value of the experimental second moment at -196 and at -185°C is $17.7 \pm 0.3 \text{ G}^2$ and decreases as the temperature increases.

When the resonance signal shows two components the second moment of the broad and the narrow components were calculated separately. For the broad gaussian line it was calculated with the relation

$$S^{\text{exp.}} = (\frac{1}{2}\Delta H_{\text{pp}})^2 \quad (2)$$

where ΔH_{pp} is the peak to peak line width obtained from the fitting. To obtain a finite value for the second moment of the narrow lorentzian line we have used the usual approximate relation ³ for a cut off lorentzian line shape

$$S^{\text{exp.}} \sim a^3 \Delta H_{\text{pp}} / \pi \quad (3)$$

where a is the cut-off distance from H_0 and ΔH_{pp} again was obtained from the fitting. We have assumed $a = 6\Delta H_{\text{pp}}$ which corresponds to a cut off distance at which the absorption signal is reduced to 2 % of its maximum value and is of the order of the noise. The second moments calculated in this way are therefore in error by about two times the error in the line-width.

At 20°C the experimental second moment reaches the value of $5.3 \pm 0.2 \text{ G}^2$ for the broad component and $3.3 \pm 0.2 \text{ G}^2$ for the narrow component. The sum of these values is in good agreement with the value $8.4 \pm 0.3 \text{ G}^2$ calculated with relation (1) for the total line. The second moment further decreases as the decomposition temperature is approached. However, it does not reach a constant value before decomposition of the substance.

The temperature behaviour of the n.m.r. signal of the sample allows the explored temperature interval to be divided into two regions: i.e., below and above room temperature. Below room temperature we have found that the behaviour is reversible. The narrow and the broad components, present at room temperature, get broader on cooling and also the narrow one disappears at the same temperature as that at which it appears on raising the temperature from -196°C . Above room temperature the behaviour is not reversible. After the decomposition of the sample, the narrow component disappears completely and does not appear on cooling again to room temperature.

The possibility of partial decomposition of the sample at room temperature, giving products with considerable freedom of motion in the lattice, was verified in another sample of $(\text{C}_8\text{H}_8)_2\text{Fe}$ in which was observed, over a wide range of temperature, a resonance signal constituted of three components: i.e., the broad component, the narrow component, and a much narrower one which was attributed to such mobile decomposition products. This second sample was recognized to be partially decomposed due to aging between the preparation and the measurements. For this reason we have reported only the measurements performed on fresh samples.

DISCUSSION

The low temperature decrease in line-width, observed in $(\text{C}_8\text{H}_8)_2\text{Fe}$, is attributed to the onset of a motional state in the crystalline lattice. Such a line-narrowing can be treated empirically by use of the relationship ⁴

$$(\Delta H)^2 = B^2 + C^2 \frac{2}{\pi} \tan^{-1} \frac{\alpha \gamma \Delta H}{2\pi \nu_c} \quad (4)$$

where ΔH is the measured line-width, ν_c the correlation frequency of the motion which can modify its rigid contribution C to the overall line-width, B the line-width at the end of the narrowing, γ the gyromagnetic ratio for protons and $\alpha = 0.18$, a constant. The rigid lattice line-width is then

$$\Delta H_{\text{rig}} = (B^2 + C^2)^{\frac{1}{2}}. \quad (5)$$

For the correlation frequency a temperature dependence of the Arrhenius type was assumed :

$$\nu_c = \nu_0 \exp(-E_A/RT) \quad (6)$$

where ν_0 is the frequency of motions for $T = \infty$ and E_A is the activation energy for the motion.

We have analysed the line-narrowing of the broad component with the relations (4) and (6). The calculations were performed using an IBM 360/44 computer and a program in FORTRAN IV. From the experimental values of ΔH were calculated the correlation frequencies. With the least square method, we have obtained the best straight line equation for a plot of $\ln \nu_c$ against $1000/T$. The values of the parameters providing this fit to the experimental data were $\Delta H_{rig} = 12.1$ G and $B = 4.8$ G. The activation energy and frequency factor obtained are $E_A = 2.6 \pm 0.1$ kcal mol⁻¹ and $\nu_0 = 5.8 \times 10^7$ s⁻¹.

Such a value for the activation energy is much smaller than that of 8.3 ± 0.4 kcal mol⁻¹ found⁵ in $(C_8H_8)Fe(CO)_3$ for the motion of the cyclooctatetraene ring in its approximate molecular plane. Since in both molecules the cyclooctatetraene rings are not planar one would expect in $(C_8H_8)_2Fe$ an activation energy of about the same magnitude for the same type of motion. The value obtained by us indicates that in $(C_8H_8)_2Fe$ rotation of the cyclooctatetraene rings cannot be invoked to explain the line-narrowing. The presence of a less hindered motion must therefore be assumed to justify the relatively low value of the activation energy.

As the broad component maintains its gaussian shape after the narrowing, while the narrow component approximates to a lorentzian shape, we must infer, following the general theory of the n.m.r. linewidth,⁴ that the correlation frequency of the motion that narrows the former must be much lower than that of the motion that narrows the latter. This is also in agreement with the different plateau values of line-width reached at the end of the narrowings.

The rigid lattice second moment S_0 for proton magnetic resonance spectra was calculated from the theory of Van Vleck⁶ for a polycrystalline sample. The intramolecular contribution to the second moment was evaluated for one of the two non equivalent molecules. The small differences between them allow us to assume the same value also for the other type of molecule.

The intramolecular contribution to the second moment is given by

$$S_1 = \frac{358.1}{N_0} \sum_j r_{ij}^{-6} \quad (7)$$

where $N_0 = 16$ is the number of protons in the molecule. The interproton distances r_{ij} are expressed in Å and were calculated, with a computer, from the positions² of the carbon atoms assuming standard bond lengths and angles; no equivalent protons exist in the molecule of $(C_8H_8)_2Fe$.

The intermolecular contribution to the second moment was broken up into two contributions: a Van Vleck sum truncated at a radius M and a terminal contribution for $r_{ij} > M$. For the truncated sum S_2 we have used an expression similar to (7) with a cut-off radius $M = 5$ Å. The terminal contribution S_3 was derived by assuming⁷ a continuous distribution of protons at large r_{ij} and replacing the sum with an integral:

$$S_3 = 358.1 \, 4\pi N_p (3M^3V)^{-1} \quad (8)$$

where $N_p = 192$ is the number of protons in the unit cell and V is the volume of the unit cell in Å³. The contribution due to iron nuclei was found to be negligible.

The theoretical calculations of the rigid lattice second moment were made neglecting effects of vibrations.^{8, 9} The evaluation of the corrections of zero-point vibrations and torsional oscillations on second moment involves the computation of averages over the various possible motions which cannot be performed effectively for substances, such as $(C_8H_8)_2Fe$, where the major contributions to the moments arise from intermolecular terms.^{8, 10} It is our opinion that, in the present case, such corrections would be of the order of the experimental error.

The results of the calculations for the rigid lattice second moment

$$S_0 = S_1 + S_2 + S_3 \quad (9)$$

are summarized in table 1 where, in the first column, are given the contributions calculated with the room temperature distances. The difference between the experimental second moment at $-185^\circ C$, $S_0^{exp.} = 17.7 \pm 0.3 \text{ G}^2$, and the value calculated for a rigid lattice with internuclear distances obtained from X-ray measurements performed at room temperature, $S_0^{calc.} = 15.22 \text{ G}^2$, can be justified taking into account the thermal contraction of the crystal cell. Due to lack of knowledge of the linear

TABLE 1.—RIGID LATTICE N.M.R. SECOND MOMENT FOR BIS(CYCLOOCTATETRAENE)IRON

	$S_0^{calc.}/G^2$ with room temperature distances	$S_0^{calc.}/G^2$ at $-185^\circ C$	$S_0^{exp.}/G^2$ at $-185^\circ C$
S_1	5.37	5.37	—
S_2	9.23	11.63	—
S_3	0.62	0.64	—
S_0	15.22	17.64	17.7 ± 0.3

expansion coefficients for $(C_8H_8)_2Fe$ we have assumed the value of $0.8 \times 10^{-4} C^{-1}$ obtained as an average over the expansion coefficients of similar compounds.¹¹ We have further assumed that the contraction of the unit cell is isotropic and that it does not modify the intramolecular distances. For this reason the intramolecular contribution S_1 maintains the same value in the two first columns of table 1. The second moment calculated with the correction for the thermal contraction is reported in the second column of table 1. The agreement between the experimental and the theoretical second moment values at $-185^\circ C$ could be actually less good if one had taken into account the effect of vibrations. In view of the relative smallness of such corrections, which would not substantially affect the agreement, we conclude that the rate of the motions presumably present below $-185^\circ C$ in the lattice is not great enough to appreciably affect the second moment. In this sense the lattice may be regarded as "rigid".

The decrease of the second moment observed at higher temperatures is attributed to motions of increasing rate that take place in the lattice. As the $(C_8H_8)_2Fe$ molecule does not possess any simple symmetry axes it was impossible to calculate the intramolecular contribution to the second moment arising from the various possible motions.

We have considered only the extreme case of general molecular reorientation of the molecules about their centre of gravity. It has been shown¹² that in this case the intramolecular contribution to the second moment vanishes and that the interproton distances r_{ij} in the Van Vleck expression (7) can be replaced by the centre-to-centre molecular distances. In this limit the second moment S_R for general reorientation of the molecule is given by

$$S_R = 358.1 N_0 \sum_i R_i^{-6} \quad (10)$$

where R_i is the centre-to-centre radius joining the molecule taken as origin and an i th nearest neighbour.

The calculated value obtained in this way, using the room temperature distances, is $S_R = 0.48 \text{ G}^2$ and is much smaller than the experimental second moment at 20°C both for the narrow and the broad components. This means that, at room temperature, no general reorientation of the molecule is achieved.

From the overall behaviour of the line-width with temperature and from the comparison of the experimental and theoretical second moment values we may conclude that the lattice, below -185°C , is "rigid" which, in the present case, means that any motion occurs at an effective frequency of less than about $5 \times 10^4 \text{ s}^{-1}$.

The broad and narrow components of the resonance signal must be associated with the existence in the lattice of two types of motion with different characteristic rates. Neither of these motions is a rotation of the cyclooctatetraene ring, nor a general reorientation of the molecule.

The simultaneous presence of a broad and a narrow component in the resonance signal has several interpretations in the literature. In those substances in which amorphous and crystalline regions coexist the narrow component has been attributed to the presence of less hindered molecular motions taking place in the former region, while the broad component to the hindered molecular motions in the latter. This interpretation cannot be accepted in the case of $(\text{C}_8\text{H}_8)_2\text{Fe}$ because it is wholly crystalline. Another interpretation of the narrow component could be related to the existence of low weight molecular fractions endowed with a great motional mobility. This interpretation too is rejected in the present case as previously pointed out. We dismiss the assumption of the existence of rotations or movements of parts of the molecule due to the absence of either freely rotating or twisting, or bending molecular fragments. As a consequence any motion must involve the whole molecule. On the basis of X-ray information, which indicates the coexistence in $(\text{C}_8\text{H}_8)_2\text{Fe}$ of ordered and disordered molecules, we believe that the broad component is associated with the ordered molecules, in which are present lower frequency motions and, consequently, an incomplete average of the dipolar proton-proton interaction, and the narrow one to the disordered molecules, in which more rapid motions are present.

Following this argument the ratio of the area of the broad component to that of the narrow one should be two to one. The ratio found by us decreases with increasing temperature and reaches the value 3.5 at 40°C . Such a result must be interpreted as an increase of the number of disordered molecules whose motion is thermally activated. From these considerations we conclude that the disorder observed at room temperature, with X-rays, is dynamic. Since rotations of the $(\text{C}_8\text{H}_8)_2\text{Fe}$ molecule as a whole or of the C_8H_8 rings are not allowed for steric reasons and would require an activation energy higher than that found, we put forward the hypothesis that the completely activated motions, observed at room temperature, are small oscillations of the rings. In the disordered molecules the C_8H_8 rings may oscillate between the two possible equilibrium positions. This is associated with the so called internuclear tautomerism observed with high resolution n.m.r. by Carbonaro *et al.*¹³ in solution and hypothesized for the crystalline state.¹ The rate of such oscillations for the disordered molecules is higher than that of the ordered ones.

The authors thank Prof. G. Allegra and Dr. A. Colombo for valuable suggestions and useful discussions. Thanks are also due to Prof. A. Carbonaro for kindly supplying the samples and to Mr. L. Cattaneo for assistance in performing the measurements.

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