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The motion of tetrahydroselenophene, C_4H_8Se , in the solid complex: $C_4H_8Se \cdot I_2$. By BJØRN PEDERSEN, *Central Institute for Industrial Research, Oslo 3, Norway* and HÅKON HOPE, *Kjemisk institutt, Universitetet i Oslo, Oslo 3, Norway*.

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Hope & McCullough (1964) have recently determined the crystal and molecular structure of the 1:1 complex which tetrahydroselenophene forms with iodine. Satisfactory agreement between the experimental and calculated X-ray data was only obtained, however, by assuming a twofold disorder of the two carbon atoms opposite the selenium atom in the five-membered ring. The tetrahydroselenophene molecule is a puckered ring as shown in Fig. 1, where adjacent methylene groups are in an approximately staggered configuration. As pointed out by the authors, and shown in the Figure, the puckering is equally probable in either of two ways, giving rise to two molecular conformations. For symmetry reasons the packing contacts of the ring are not changed in going from one configuration to the other. Hence, no strong barrier is apparent, which would prevent interchange of the two forms even in the solid, and Hope & McCullough therefore ascribed the observed disorder to such an interchange. To get more conclusive evidence about the nature of the apparent disorder it was decided to study the solid complex with wide-line proton magnetic resonance techniques, and in this note we will give the results of the study.

The shape of the proton magnetic resonance spectrum of a solid at a given temperature is determined by the distribution and relative motion of the magnetic nuclei, mainly the protons, in the solid. It is not possible to calculate in detail the observed spectrum from a given distribution of nuclei, but, as shown by Van Vleck (1948), the second moment of the spectrum taken about the midpoint is given by the following expression, which is valid for a static configuration of nuclei:

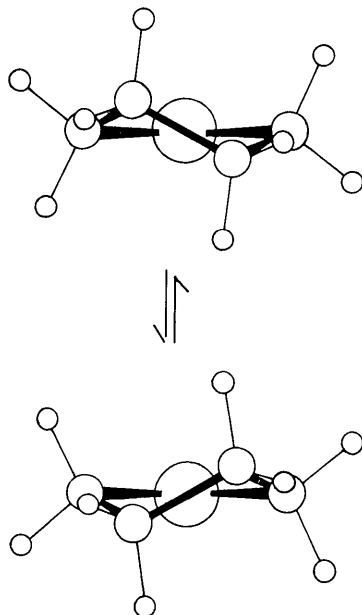


Fig. 1. View of the two possible conformations of the tetrahydroselenophene molecule.

$$M_2 = \int_{-\infty}^{\infty} h^2 g(h) dh \\ = N^{-1} (3\mu/2)^2 \sum_{kj} [r_{kj}^{-3} (3 \cos^2 \theta_{kj} - 1)]^2 \\ + \frac{1}{2} N^{-1} \sum_{k,i} \mu_i^2 \frac{I_i + 1}{I_i} [r_{ki}^{-3} (3 \cos^2 \theta_{ki} - 1)]^2. \quad (1)$$

Here $g(h)$ is the normalized shape function and $h = H - H_0$, where H is the value of the external field and H_0 its value at resonance. μ is the proton magnetic moment, r_{kj} is the distance from the proton k to the proton j , θ_{kj} is the angle between r_{kj} and H , and r_{ki} is the distance from the proton k to the nucleus i , carrying the magnetic moment μ_i and spin I_i . The summation is taken over all pairs of the N nuclei in the sample. Because the contribution from a neighbor decreases as the inverse sixth power of the distance, only neighbors within about 5 Å from a given proton will give a significant contribution to the theoretical second moment. We can therefore, in this case, omit the second term in equation (1), and in the first term the intramolecular contribution, M_{2a} , will give the main contribution to the second moment.

$$M_{2a} = n^{-1} (3\mu/2)^2 \sum_{kj} [r_{kj}^{-3} (3 \cos^2 \theta_{kj} - 1)]^2. \quad (2)$$

Here n is the number of protons in one molecule, and the summation is carried out over all proton pairs in the molecule. For a powder sample, where the molecule can take all orientations, equation (2) reduces to

$$M_{2a} = 4/(5n) (3\mu/2)^2 \sum_{kj} r_{kj}^{-6}. \quad (3)$$

As stated above, equations (2) and (3) are valid only for a static configuration of protons. If the molecule can jump back and forth between two conformations with a certain frequency, ν_x , this type of motion will affect the shape of the proton magnetic resonance spectrum. It is known from general nuclear magnetic resonance theory (Abragam, 1961) that when the frequency of motion, ν_x , is much smaller than a characteristic frequency, approximately the square root of the second moment expressed in $c.sec^{-1}$, the configuration can be regarded as static and the second moment is given by equation (3). When the frequency of motion is much larger than this characteristic frequency, which usually is of the order of 10 $kc.sec^{-1}$, the spectrum will be motionally narrowed, and the second moment is not given by equation (3). In our case, where the molecule is assumed to be oscillating between two conformations, the second moment can be shown to be given as

$$M_{2m} = 1/(5n) (3\mu/2)^2 \sum_{kj} [r_{kj}^{-6} + r'_{kj}{}^{-6} + r_{kj}^{-3} r'_{kj}{}^{-3} \\ \times (3 \cos^2 \beta_{kj} - 1)]. \quad (4)$$

This equation is valid for a powder, *i.e.* we have averaged over all orientations. The distance between the protons k and j is r_{kj} in one conformation, and r'_{kj} in the other. β_{kj} is the angle between r_{kj} and r'_{kj} . If $r_{kj} = r'_{kj}$ the second moment is simply

$$M_{2m} = 1/(5\pi) (3\mu/2)^2 \sum_{kj} (3 \cos^2 \beta_{kj} + 1) r_{kj}^{-6}. \quad (5)$$

The atomic positions of the protons were not given by Hope & McCullough (1964), but a set of likely positions has been obtained by assuming that the carbon-hydrogen bond distance is 1.08 Å and the H-C-H angle is 109.5°. By means of these positions the second moment for the static case [equation (3)] and the fast oscillating case [equations (4) and (5)] have been calculated, and the results are given in Table 1.

Table 1. *Experimental and theoretical second moments for a static and flipping C₄H₈Se molecule*

Case	Theoretical second moment	Experimental second moment
Static	17.6 G ²	19 ± 2 G ²
Flipping	8.4	8.5 ± 1

The proton magnetic resonance spectra of C₄H₈Se · I₂ held at several temperatures from room temperature down to liquid nitrogen temperature were recorded on a Varian Asc. Dual Purpose Spectrometer operating at 60 Mc.sec.⁻¹. The room temperature spectra were definitely narrower than the spectra obtained at liquid nitrogen temperature (Fig. 2). When the sample is cooled from room temperature the spectrum begins to broaden at about -70 °C, and the broadening is completed at about -140 °C. At these low temperatures the signal is easily saturated, indicating that the spin-lattice relaxation time gets longer as the temperature is decreased. To avoid saturating the signal we had to work at a low r.f. power level, resulting in a relatively poor signal to noise ratio. The spectrum also changes shape in the transition region from a simple bell shaped curve at room temperature to a broadened two-peak spectrum at low temperatures. For these two reasons we have not tried to evaluate an activation energy from the temperature dependence of the spectrum, as the accuracy using the standard procedure will be questionable. The second moments of a set of room temperature spectra and of a set of spectra obtained with the sample in liquid nitrogen have been evaluated, and the results are given in Table 1. The liquid nitrogen second moment is compared with the theoretical second moment calculated for a rigid molecule, and the room temperature second moment with the motionally averaged theoretical second moment.

All these observations give a consistent picture of the motion of the tetrahydroselenophene molecules in the solid iodine complex in accordance with the ideas of Hope &

McCullough (1964). The observed temperature dependence of the spectrum shows that the molecule is oscillating between two equivalent conformations with a thermally activated motion, which is slower than 10 kc.sec.⁻¹ below -140 °C and faster than this above -70 °C. The proton spin system is very likely relaxed by means of this oscillatory motion, explaining why the signal was easily saturated at low temperatures. The broadened two-peak spectrum obtained at low temperatures is due to the fact that the protons are grouped in pairs, methylene groups, in the molecule (Pake, 1948). The main contribution to the second moment, 11.6 G², is given from this strong intra-pair interaction. When the molecule is oscillating fast, however, this interaction is greatly reduced, explaining the observed bell-shaped curve without any fine structure at high temperatures. Finally, the good agreement between the observed and calculated second moments given in Table 1 also more quantitatively supports the proposed model of the molecular motion.

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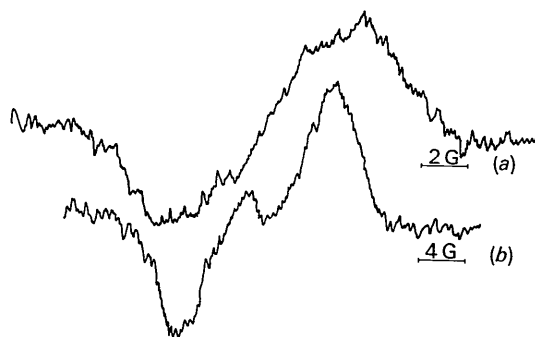


Fig. 2. The proton magnetic resonance spectra of C₄H₈Se · I₂ at (a) room temperature and (b) -200°C. Note the difference in scale.

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Compound tessellations in crystal structures. By HIROSHI TAKEDA* and J. D. H. DONNAY, *Crystallographic Laboratory, The Johns Hopkins University, Baltimore, Maryland, U.S.A.*

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Introduction to tessellations

A *regular tessellation* (Coxeter, 1961, p. 61) is an assemblage of equal regular polygons that cover the plane without

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overlap or interstice. Schläfli proposed the symbol $\{p, q\}$ to designate a tessellation of p -gons, q of which meet at each vertex. There are three regular tessellations. The vertices of $\{4,4\}$ are the nodes of a primitive square net; those of $\{3,6\}$ form a primitive hexagonal net. The vertices of $\{6,3\}$, on the other hand, do not make a net: they illustrate the structure