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Molecular motion in iso-butyl bromide by N.M.R.

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Résumé

Il est montré par résonance magnétique nucléaire à *basse* résolution des protons que pour la molécule de bromure d'isobutyle, la forme dite « gauche » est légèrement plus stable que l'autre forme. On trouve que l'un des groupements « méthyl » est beaucoup plus libre à réorienter que l'autre. Les résultats sont en bon accord avec des mesures diélectriques pour le liquide surfondu comme pour le cristal.

1. Experimental.

The proton magnetic resonance absorption in iso-butyl bromide [$(CH_3)_2 CHCH_2 Br$], both in the crystalline form and as a supercooled liquid has been measured over the temperature range — 196° C to — 115° C. The measurements were made at a resonant frequency of 15 Mc/s using an autodyne spectrometer.

On cooling below its melting point (— 118° C) iso-butyl bromide normally forms a supercooled liquid, however, by suitable temperature control it is possible to grow a crystal. During formation of the crystal the broad crystal line grows at the expense of the narrow liquid line and it is possible to obtain any desired proportion of crystal to liquid. The percentage of crystal present was deduced from the nuclear resonance absorption derivative curves which show the two signals clearly distinguished (examples will be shown at the Conference).

2. Interpretation.

The absorption lines had no structure and our interpretation is therefore based primarily upon the second moment values. For protons and for a

crystalline (or amorphous) mass, the second moment of the absorption line is [1]:

$$\Delta H_2^2 \text{ (rigid)} = \frac{720}{N} \sum_{i>j} R_{ij}^{-6} \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where

N = number of protons interacting

R_{ij} = proton separation in Å.

This is for a " rigid " lattice. Any motion that is sufficiently rapid to narrow the line reduces the experimental second moment in a calculable manner. The figure shows the variation of the second moment with temperature.

(a) *Second moment for the rigid lattice.*

Iso-butyl bromide can exist in two isomeric forms which we call the *Trans* and *Gauche* configuration (see diagram), and the corresponding second moment values have been calculated. The intramolecular contribution for *both* isomers is 22.5 gauss^2.

The intermolecular contribution is difficult to estimate but due to the high proton concentration it is reasonable to assume that each proton has roughly three proton neighbours at the van der Waals distance of 2.4 Å. The theoretical value for the rigid lattice second moment is therefore ΔH_2^2 (rigid) = 28.1 gauss^2 for *trans* and *gauche*.

By experiment:

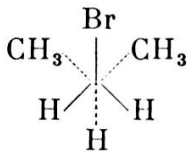
ΔH_2^2 (rigid) = 29 gauss^2 for the liquid and
31 gauss^2 for the crystal.

The agreement between experimental and theoretical values is satisfactory in view of the difficulty in estimating the intermolecular contribution.

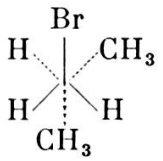
The crystal is expected to have a rather higher second moment as observed due to the more ordered arrangement and hence closer packing of the protons.

(b) *The isomeric forms of iso-butyl bromide.*

General results [2] on similar molecules suggest that there are only two distinct isomers of this molecule



Trans



Gauche

Little relevant spectroscopic data is available on iso-butyl bromide [3, 4] but it is known that iso-butyl chloride exists in both forms in the liquid state [5] although which is the lower energy form has not been determined. In *n*-propyl bromide ($CH_3\,CH_2\,CH_2\,Br$) the *trans* form is the most stable in the crystalline phase [6], but in the liquid the energy difference is small [7].

Iso-butyl bromide can be obtained from *n*-propyl bromide by replacing a proton by a methyl group, but then *trans n*-propyl bromide becomes *gauche* iso-butyl bromide, hence, unless substitution changes the intramolecular forces, the *gauche* form of iso-butyl bromide is the more favoured.

This conclusion is supported by nuclear magnetic resonance measurements as shown below.

(c) *Limited motional narrowing.*

The liquid line narrows to 18 gauss^2 at — 165° C with a transition centered at — 175° C and the crystal line narrows to a slightly smaller value centred about — 160° C and continues to fall slowly until the melting point at — 118° C. We believe that the first narrowing is due to CH_3, C_3 reorientation. The calculated second moments for one or two CH_3 groups per molecule in effective motion are,

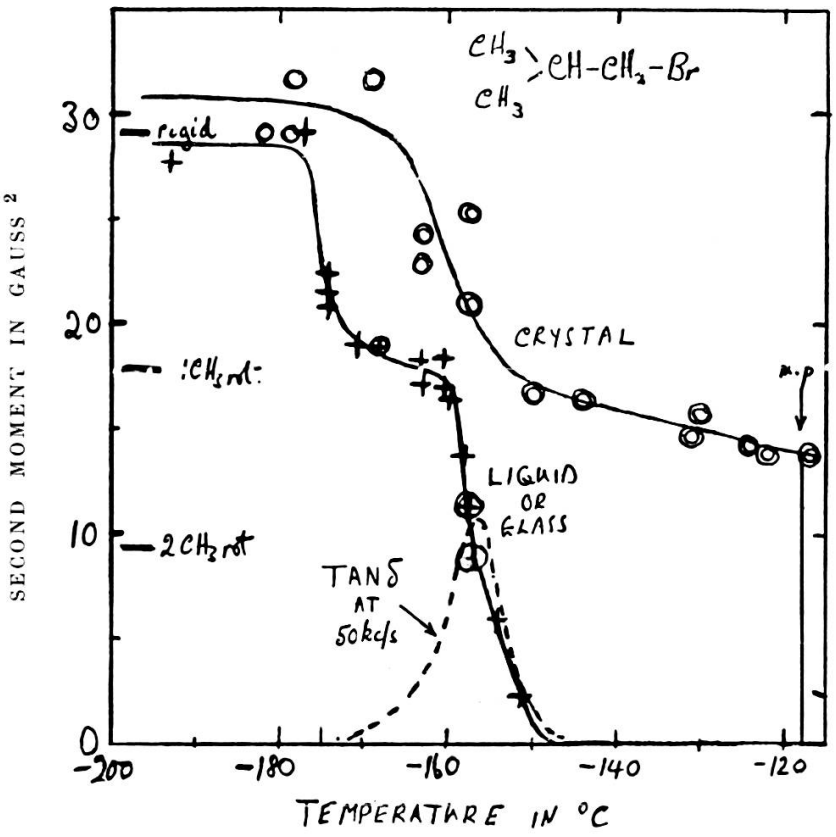
$$\Delta H_2^2 \text{ (motion)} \quad \begin{array}{l} \text{one } CH_3 — 18.8 \text{ gauss}^2 \\ \text{two } CH_3 — 10.6 \text{ gauss}^2 . \end{array}$$

Hence at — 165° C close to 50% of the methyl groups are in effective rotation. This is most likely due to each molecule having *one* of its two methyl groups reorienting.

The closest approach of the bromine atom to the nearest proton in a methyl group using the model in the diagram is 2.5 Å whereas the sum of the bromine and hydrogen van der Waals radii is 3.15 Å. This suggests that in the *trans* form, the rotation of both methyl groups may be seriously hindered by the bromine, whereas only one is blocked in the *gauche* form. The nuclear magnetic resonance results indicate that one CH_3 group reorientates much more rapidly than the other. This therefore favours

the view that the *gauche* configuration is the more stable isomer, possibly by a few hundred cal/mole [9].

The crystal line width transition occurs some 15° C higher and may be interpreted in the same way. The higher transition temperature may be due to slightly larger intermolecular forces due to closer packing.



(d) *The severe narrowing region.*

The severe narrowing about — 157° C in the supercooled liquid is so great as to require thermal reorientation of the molecule as a whole. This is supported by dielectric measurements [8] which reflect the reorientation of the C-Br bond. The dielectric tan δ at 50 kc/s as a function of temperature is shown on the figure [8] and the correlation is excellent. The whole of the line narrows so that all the protons take part in the motion with very similar correlation times, i.e. the whole molecule and all the molecules move.

There is no severe narrowing in the crystal line below the melting point which means that molecular reorientation if any, at a rate is less than

50 kc/s. In accord with this, dielectric measurements show no dipolar contribution for frequencies down to 500 c/s [8]. Presumably reorientation is prevented by larger intermolecular forces caused by more regular packing of the molecules in the crystal. A detailed account of this work will appear elsewhere [9].

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