STRUCTURAL IMPLICATIONS OF THE [115]In NUCLEAR QUADRUPOLE RESONANCE SPECTRUM OF CH_3InI_2
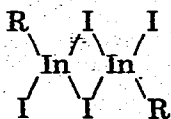
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Summary

Based on its vibrational spectrum, CH_3InI_2 has been proposed to contain linear $In(CH_3)_2^+$ ions rather than being a bridged halogen dimer as is found for most other compounds of this type. The [115]In nuclear quadrupole resonance spectrum observed here for CH_3InI_2 yields a coupling constant of 1270.6 MHz and an asymmetry parameter of 0.051 ± 0.006. The small asymmetry parameter is additional evidence of an axially symmetric environment for indium, such as $In(CH_3)_2^+$, and by comparison to In_2I_6 strongly suggests that the dimeric structure is not present.

Recently, the synthesis of CH_3InI_2 by oxidative addition of CH_3I to InI has been reported [1—3]. Unlike other Group IIIA halides and organohalides of this type which contain halogen-bridged dimers or are weakly polymeric in the solid state [4], the ionic formulation, $[In(CH_3)_2]^+[InI_4]^-$, was proposed for CH_3InI_2. This suggested structure was based on the vibrational spectrum [1—3]. Hobbs and Tobias also reported the existence of $(CH_3)_2In^+$ in aqueous solution [5]. The mass spectrum of CH_3InI_2 studied by Gynane et al. [2], showed the parent peak to be a dimer which would likely have the following structure:

$$\begin{array}{ccccc} R & & I & & I \\ & \diagdown & \Big/ \diagdown & \Big/ & \\ & \text{In} & & \text{In} & \\ & \diagup & \diagdown \diagup & \diagdown & \\ I & & I & & R \end{array}$$

This parent ion was not found by Poland and Tuck [3].

Nuclear quadrupole resonance data could greatly aid in clarifying the structure in the solid state because both [115]In ($I = 9/2$) and [127]I ($I = 5/2$) are quadrupolar nuclei and their spectra in the salt form will be very different from those in the bridged dimer form. A complete [115]In spectrum would yield four resonances for each type of indium atom present. For [127]I, two signals will re-

TABLE 1

^{115}In AND ^{127}I NUCLEAR QUADRUPOLE RESONANCE DATA (MHz) AND ASYMMETRY PARAM-
ETERS IN In$_2$I$_6$^{a} AND CH$_3$InI$_2$ AT 25°C^b

^{115}In						
	1/2↔3/2	3/2↔5/2	5/2↔7/2	7/2↔9/2	e^2Qq/h	η
In$_2$I$_6$	37.506	29.986	36.265	51.238	320.41	0.69
CH$_3$InI$_2$	54.36(10)	105.55(35)	158.68(10)	211.65(5)	1270.6	0.051 ± 0.006

^{127}I				
	1/2↔3/2	3/2↔5/2	e^2Qq/h	η
In$_2$I$_6$	122.728	229.190	772.43	0.237^c
	173.177	346.289	1154.3	0.0^d
	173.633	347.234	1157.4	0.0^d
CH$_3$InI$_2$	—	—	—	—

^{a} References 6—9. ^{b} Parenthetical numbers are signal-to-noise ratios. ^{c} Bridging iodine atom. ^{d}Terminal iodine atom.

sult from each type. Although very little ^{115}In NQR spectroscopy has been re-
ported, the ^{115}In and ^{127}I frequency in In$_2$I$_6$ [6—9] and some additional organo-
indium halide data [10] have been obtained. The nuclear quadrupole coup-
ling constants, e^2Qq, and asymmetry parameters, η, for In$_2$I$_6$ are reported in
Table 1. With these data and the comparative effects in the analogous AlX$_3$
and RAlX$_2$ compounds [11], predictions can be made regarding the spectrum
of CH$_3$InI$_2$ if the dimeric structure shown above is present in the solid state.
Two rather widely separated resonance pairs for iodine corresponding to brid-
ging and terminal iodine atoms should be observed. The lower frequency pair
will have a reasonably large asymmetry parameter as a result of the coordinate
geometry of the bridging halogen. The terminal halogens will have negligible
asymmetry because of their axial symmetry. The indium resonances would
show a large asymmetry paramter much like that found in In$_2$I$_6$ [6—9] and
in the analogous aluminum compounds [11].

    If the ionic formulation of [In(CH$_3$)$_2$]$^+$[InI$_4$]$^-$ is present in the solid state
only one set of iodine signals will be observed (assuming no crystallographic
inequivalence) and η will be close to zero. For ^{115}In the cation will produce one
set of signals yielding ideally zero asymmetry. The anion would give no ^{115}In
signals because of the tetrahedral arrangement of iodine atoms about indium
[2, 3].

    CH$_3$InI$_2$ was prepared as before [1—3]. Colorless highly crystalline material
was obtained by dissolving the compound in CH$_3$I and evaporating the solution
over a period of three days using a slow stream of nitrogen. The Raman and mass
spectra were recorded and confirmed the compound to be the same as that ob-
tained previously [1—3]. The NQR spectrometer system has been described
before [12]. A Wilks OS-4A cavity oscillator was used to scan the 270-350
MHz region.

    The results are reported in Table 1. No other signals were found in the
10 - 350 MHz region. The resonances at 105.55, 158.68 and 211.65 MHz are
in the region of ^{127}I resonances for this type of compound. However the 105.55
and 211.65 MHz signals cannot belong to the same iodine atom because ν (3/2 ↔ 1/2)
must be greater than or equal to one-half ν (5/2 ↔ 3/2). The difference between

2(105.55) and 211.65 is not great but is at the very outer limit of the experimental uncertainty in the numbers (± 0.08%). Further, no high frequency counterpart for the resonance at 158.68 MHz was observed. In fact, it is extremely unlikely that any of these resonances belong to iodine because all four signals fit the eigenvalue equation* for $I = 9/2$ and $\eta = 0.051 \pm 0.006$ with an uncertainty of 0.08% in the coupling constant. Since the fit of frequencies to the eigenvalue solutions is very sensitive for $I = 9/2$, all four resonances were determined to belong to ^{115}In. The low asymmetry at indium implies that the bridged formulation represented above and found in RAlX$_2$ compounds [11] and In$_2$I$_6$ [6—9] does exist in CH$_3$InI$_2$, and that the ionic structure [In(CH$_3$)$_2$]$^+$ [InI$_4$]$^-$, or a polymeric bridged structure in which the indium atom has axial symmetry as suggested previously [1—3], must be present. The very large coupling constant, (the largest reported to date for ^{115}In), is also consistent with an indium site in which the largest component of the electric field gradient tensors for the external groups adds rather than cancels at In. A linear arrangement for the CH$_3$ groups about indium would result in such an occurrence.

It would be valuable to observe the ^{127}I resonances to have a better understanding of their environment but regretfully none were observed. Such signal absences are not uncommon in NQR spectroscopy and probably result from unfavorable nuclear relaxation conditions for those atoms.

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*The eigenvalue equation for $I = 9/2$ given in ref. 13 was solved for values of the asymmetry parameter, η, in increments of 0.001 using a computer program written by L.F. Hamilton in this laboratory.