A Comparison of Nuclear Quadruple Resonance and Mössbauer Spectra of Tin Halides

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WE present some n.q.r. and Mössbauer spectral data on organotin bromides and iodides (Tables 1—3); all data were obtained at 77°K.

The empirical equation (1) describes the

$$\nu\,(^{81}\text{Br}) = 164{\cdot}24 - 19{\cdot}06\,\Delta\ (\text{Mc./sec.}) \qquad (1)$$

correlation of the bromine n.q.r. frequency, ν (averaged over the crystallographic splittings) with tin quadrupole splittings, Δ, in the Mössbauer spectra of bromides R_3SnBr (R = Br, Ph, Et). The equation (1) makes possible the evaluation of the range of n.q.r. frequencies for tin compounds not yet studied—making use of the Mössbauer data—and *vice versa.*

A similar trend in the variation of quadrupole coupling constants in n.q.r. and Mössbauer spectra seems reasonable, since we are considering the bonded atoms and variations of electric field gradient at both nuclei are mainly caused by a redistribution of *p*-electrons of the two atoms concerned.

The nature of the relationship between n.q.r. frequencies and isomer shifts of R_3SnBr compounds is more complicated, and we can only say that changes of $\delta(\Delta)$ are monotonic (see Tables 1 and 2).

An empirical approach to the problem of a correlation between the electric field gradient and

TABLE 1

Quadrupole frequencies ν

Compound	ν (^{79}Br) (Mc./sec.)	s/n	ν (^{81}Br) (Mc./sec.)	s/n	ν$_{av}$(^{81}Br) (Mc./sec.)
$SnBr_4$[3]			165·270		164·78
			165·401		
			165·208		
			162·032		
Ph_3SnBr	141·82	2	118·44	8	117·44
	139·77	2	116·44	8	
Et_3SnBr	118·77	6	99·23	6	99·23
Et_2SnBr_2	134·88	5	112·68	10	109·01
	128·35	10	107·18	20	
$SnBr_2$	133·94	1·5	111·86	3	
			126·31	6	
			139·03	3	

TABLE 2

Mössbauer spectral parameters

	Compound	Δ (mm./sec.)	δ (α-Sn) (mm./sec.)
(1)	$SnBr_4$	0·0	−1·08
(2)	$(C_6F_5)_3SnBr$	1·60	−0·84
(3)	$(C_6H_4{\cdot}CF_3)_3SnBr$	1·94	−0·88
(4)	Ph_3SnBr	2·40	−0·70
(5)	$(PhCMe_2CH_2)_3SnBr$	2·65	−0·68
(6)	Pr_3SnBr	2·92	−0·64
(7)	$(C_2H_4CN)_3SnBr$	3·04	−0·62
(8)	Bu_3SnBr	3·30	−0·50
(9)	Me_3SnBr	3·40	−0·65
(10)	Et_3SnBr	3·45	−0·48

Values of isomer shift given relative to α-Sn. Δ and δ values are ±0·05 mm./sec. To convert to the energy scale (ev), Δ and δ must be multiplied by $7{\cdot}9 \times 10^{-8}$. Data for compounds (2), (3), (5), and (7) taken from ref. 4.

electronic structure is completely justified by the recent state of the theory. That is why a correlation between n.q.r. and quadrupole coupling constants in Mössbauer spectra of tin compounds with Hammett–Taft σ-constants is of great interest. Some correlations between n.q.r. frequencies and reaction constants σ_I, σ_c, and σ^* [1] have been found, but correlation between these constants and quadrupole splittings in Mössbauer spectra of tin compounds has not been reported previously.

An approximate correlation between ^{81}Br n.q.r. frequencies and Taft σ^* induction constants[2] has been found for R_3SnBr (R = Br, Ph, Et) (equation (2).

$$\nu = 102{\cdot}55 + 7{\cdot}48\ \Sigma\sigma^*\ \text{(Mc./sec.)} \qquad (2)$$

A similar equation for quadrupole splitting in Mössbauer spectra of the tin compounds R_3SnBr (R = Ph, Br, Me, Et,‡ Pr, Bu) is given in equation (3).

$$\Delta = 3{\cdot}15 - 0{\cdot}38\ \Sigma\sigma^*\ \text{(mm./sec.)} \qquad (3)$$

In the ν ($\Sigma\sigma^*$) and Δ ($\Sigma\sigma^*$) dependencies studied, the dominant influence of the inductive effect of the substituents upon the change in the quadrupole constants is evident.

It is interesting to note that the n.q.r. frequency for Et_2SnBr_2 does not obey equation (2). This could be explained either by the different symmetry of the molecule as compared with R_3SnBr, resulting in different additive contributions caused by the atom matrix polarisation, or by the difference in intermolecular interactions. We may assume that a correlation between σ constants and coupling constants in n.q.r. and Mössbauer spectra either proves the absence of any intermolecular interactions or indicates that such interactions are constant.

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‡ σ_I values for the ethyl group have been calculated from the equation $\sigma_I = (\sigma^* - 0{\cdot}49)/6{\cdot}23$ (ref. 2).

TABLE 3

N.q.r. and Mössbauer spectra of organotin iodides

Compound	$\nu\,(\frac{1}{2}-\frac{3}{2})$ (Mc./sec.)	$\nu\,(\frac{3}{2}-\frac{5}{2})$ (Mc./sec.)	η (%)	*eQq* (Mc./sec.)	Δ (mm./sec.)	δ (α-Sn) (mm./sec.)
SnI_4[5]	209·133	418·257	0·5	1394·19	0·0	−0·62
	207·683	415·320	1·0	1384·64		
Ph_3SnI	153·75	—	—	—	2·05	−0·79
Et_2SnI_2	149·40	293·30	12·2	980·56	3·21	−0·33

The approximate equation for quadrupole splitting values in the Mössbauer spectra of R_3SnBr (R = Br, Me, Et, Ph)‡—the inductive and resonance constants[2] of the substituents are included—is given as equation 4.

$$\Delta = 2{\cdot}97 - 1{\cdot}74\Sigma\sigma_I + 0{\cdot}22\ \Sigma\sigma_c \text{ (mm./sec.)} \qquad (4)$$

An analogous equation for ^{81}Br frequencies in R_3SnBr (R = Br, Et, Ph) is given as equation (5).

$$\nu = 103{\cdot}23 + 40{\cdot}61\ \Sigma\sigma_I - 16{\cdot}64\ \Sigma\sigma_c \text{ (Mc./sec.)} \qquad (5)$$

From the ratio of the $\Sigma\sigma_I$ and $\Sigma\sigma_c$ coefficients in these equations, it is clear that the contribution of an inductive term is much more than that of a resonance term. This fact justifies a comparison of the quadrupole splittings with the constants. It should be noted, however, that the Sn–I bond in Et_2SnI_2 has a pronounced π-bond character (Table 3) since the asymmetry parameter calculated from n.q.r. frequencies amounts to 12·2%.

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