A Convenient Means of predicting the Position of the ^{75}As Quadrupole Resonance in Co-ordination Compounds

By Gérard Jugie,* Marcel Durand, Juan Ribas, and René Mathieu

(*Laboratoire de Chimie de Coordination du C.N.R.S.*, 205 *route de Narbonne*, 31400 *Toulouse, France*)

Summary A linear correlation between the proton internal shifts (Δ_{int}) and the ^{75}As quadrupole frequencies is presented for a number of triethylarsine adducts which allows the estimation of the position of unknown ^{75}As quadrupole resonance patterns.

The potential of nuclear quadrupole resonance (n.q.r.) in affording an excellent means of estimating charge-transfer in co-ordination compounds has already been recognized for some group 3 and 5 elements.[1] Therefore the scarcity of data in the field of arsine adducts is surprising in view of the suitability of the nuclear constants of ^{75}As and the 100% natural abundance of this isotope; in our opinion, application of n.q.r. spectroscopy to this class of compounds has been limited by the difficulties in searching for unknown ^{75}As signals over a very wide frequency area without any *a priori* idea of their position.

We recently realized that in triethylarsine adducts the knowledge of an easily accessible parameter such as the proton internal shift of the ethyl group [$\Delta_{int} = \delta\,(CH_2) - \delta\,(CH_3)$] would be sufficient to give a very reliable estimate of an unknown ^{75}As signal position. We have located arsenic resonances for a series of complexes with representative group 3 Lewis acids (BH_3, BCl_3, $AlCl_3$, and $GaCl_3$) and found that the set of their ^{75}As quadrupole frequencies was approximately linearly related to the proton Δ_{int} chemical shifts of the ethyl radical; in conjunction with these results, other results for transition-metal complexes then provide a well substantiated proof of the validity of the correlation between the two parameters and prompt us to publish the plot in the Figure, the use of which will thus avoid, in most cases, the time-consuming part of the signal localisation process.

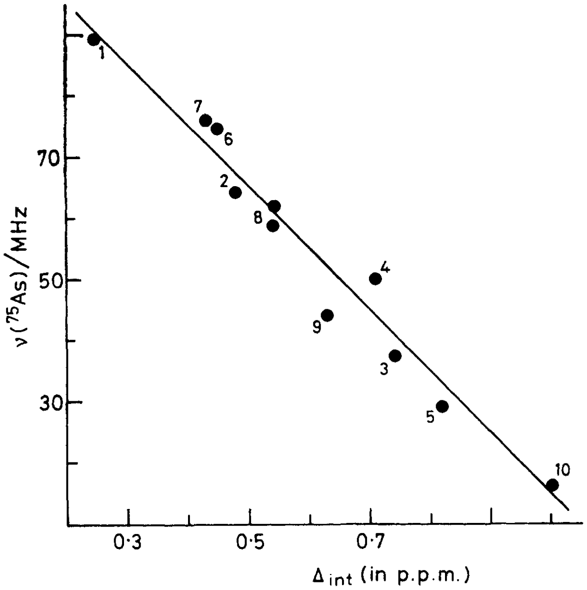

FIGURE. Plot of ^{75}As n.q.r. frequencies against ^{1}H n.m.r. internal shifts in adducts of triethylarsine. The numbers refer to the compounds shown in the Table.

In the Figure, the ^{75}As n.q.r. frequencies are plotted against the n.m.r. Δ_{int} values and the equation of the least-squares straight line through the data is $\nu(^{75}\text{As})/\text{MHz} = -101\,\Delta_{int}$ (in p.p.m.) $+116$. Qualitatively, a clue to the existence of this correlation lies in the fact that the variations of both parameters [Δ_{int} and $\nu(^{75}\text{As})$] are known[2,3] to be directly dependent upon the electronic charge transferred by the donor atom along the co-ordination bond to the Lewis acid. Using the classical Townes and Dailey treatment[4] for molecules of the type R_3MY in which the central atom (M = As) forms identical bonds with three like substituents (R = Et) and the unique bond to a fourth group (Y = acceptor) lies along the threefold axis of symmetry, the ^{75}As frequency values furnish reasonable

TABLE. ^{1}H N.m.r. and ^{75}As n.q.r. data.

No.	Compound	δ (CH$_2$)[a]	δ (CH$_3$)[a]	Δ_{int}[a]	ν (^{75}As)[b]/MHz	*a*[c] (electrons)	c.t. (electrons)
(1)	Et_3As	$1{\cdot}3_7$	$1{\cdot}1_2$	$0{\cdot}2_5$	89·61[d]	2·0	—
(2)	$Et_3As.BH_3$	$1{\cdot}6_6$	$1{\cdot}1_8$	$0{\cdot}4_8$	64·21	1·3	0·7
(3)	$Et_3As.BCl_3$	$2{\cdot}1_1$	$1{\cdot}3_7$	$0{\cdot}7_4$	37·62	1·2	0·8
(4)	$Et_3As.AlCl_3$	$2{\cdot}0_3$	$1{\cdot}3_2$	$0{\cdot}7_1$	50·15	1·2	0·8
(5)	$Et_3As.GaCl_3$	$2{\cdot}2_1$	$1{\cdot}3_9$	$0{\cdot}8_2$	29·34	1·1	0·9
(6)	$(CuEt_3AsCl)_4$	$1{\cdot}6_5$	$1{\cdot}2_0$	$0{\cdot}4_5$	74·83	1·3	0·7
(7)	$(CuEt_3AsBr)_4$	$1{\cdot}7_3$	$1{\cdot}3_0$	$0{\cdot}4_3$	76·06	1·3	0·7
(8)	$(PhC{\equiv}CPh)Co_2(Et_3As)_2(CO)_4$	$1{\cdot}2_0$	$0{\cdot}6_6$	$0{\cdot}5_4$	61·94 58·87	$1{\cdot}2_5$	$0{\cdot}7_5$
(9)	$Co_2(Et_3As)_2(CO)_6$	$1{\cdot}8_8$	$1{\cdot}2_5$	$0{\cdot}6_3$	44·13	1·2	0·8
(10)	$[Co(Et_3As)_2(CO)_3][BPh_4]$	$2{\cdot}3_2$	$1{\cdot}3_2$	$1{\cdot}0_0$	15·92[e]	1·1	0·9

[a] In chloroform solution, except for (8) (dichloromethane) and (10) (acetone); δ values are quoted with respect to internal Me_4Si, and Δ_{int} values are in p.p.m. [b] Measurements at 273 K. [c] Calculated from standard Townes–Dailey equations, assuming that the asymmetry parameter is close to zero and that a purely covalent bond is formed between arsenic and carbon in both the tri- and tetra-co-ordinated species. [d] Ref. 5; at 77 K. [e] Data obtained at 77 K.

estimates of the occupation number of what was originally the lone-pair orbital of the arsenic atom (*a*, see Table) and, in consequence, the charge transferred (c.t., see Table) to the acceptor on complexation.

Furthermore, it should be noted that preliminary temperature-dependence examinations of the ^{75}As lines of several of these adducts reveal very unusual behaviour (changes in multiplicities, pronounced reversals in slope, *etc.*). Detailed studies of these remarkable phenomena are in progress.

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