

⁷⁵As Nuclear Quadrupole Resonance in Some Arsenic Ring Compounds

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Abstract

⁷⁵As nuclear quadrupole resonance has been observed in a number of cyclic and heterocyclic organo-arsenic compounds. In cases where the structure has been determined, the multiplicity of the resonances agrees with the number demanded by the structure. Where the structure has not been determined the results indicate the existence of certain molecular symmetry elements in the solid state.

During an investigation by one of us (P.S.E.) into the synthesis and structure of heterocyclic arsenic compounds, sufficient quantities of a number of both cyclic and heterocyclic arsenic compounds were prepared to make feasible the measurement of their ⁷⁵As nuclear quadrupole resonance (n.q.r.) spectrum.

Since ⁷⁵As has spin $I = 3/2$, there is only one transition per non-equivalent site and it is not possible from a measurement of the n.q.r. frequency ν_Q to separate the coupling constant from its asymmetry parameter in a polycrystalline specimen without a detailed examination of the line shape. This was not possible with the present spectrometer.

The n.q.r. lines were located using a Zeeman-modulated noise-controlled super-regenerative oscillator spectrometer of standard design. For accurate measurement of the line position an uncontrolled Nuvistor super-regenerative oscillator working at low quench frequencies was used as described previously.¹ Frequency measurements were made with a spectrum analyser, r.f. signal generator and frequency counter.²

N.q.r. frequencies were measured when possible at 298, 195 and 77 K, and the results are listed in Table 1.

The preparation of the cyclic compounds (AsC₆H₅)₆ (1) and (AsC₆F₅)₄ (2) is described in the literature.^{3,4} The heterocyclic compounds 1,2-diphenyl-3,4-bis(trifluoromethyl)-1,2-diarsacyclobut-3-ene (3) and 1,2-bis(pentafluorophenyl)-3,4-bis(trifluoromethyl)-1,2-diarsacyclobut-3-ene (4) were prepared by treatment of the appropriate cyclic arsine (AsC₆F₅)₄⁴ or (AsC₆H₅)₆³ with excess hexafluorobut-2-yne at 160°C.

The X-ray crystal structure determination³ for arsenobenzene has shown that the molecule exists in the solid as a six-membered ring of arsenic atoms in the chair form

¹ Bastow, T. J., and Whitfield, H. J., *J. inorg. nucl. Chem.*, in press.

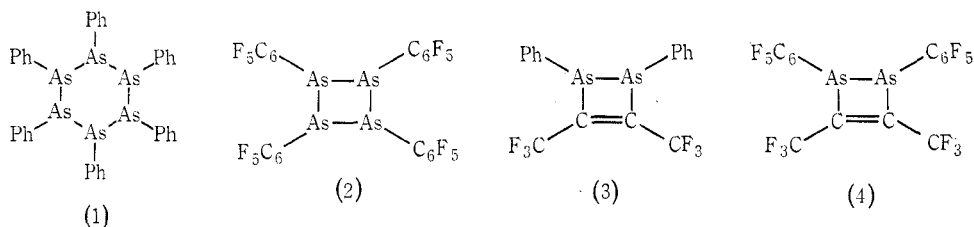
² Bastow, T. J., and Whitfield, H. J., *Solid State Commun.*, 1972, **11**, 1015.

³ Hedberg, K., Hughes, E. W., and Waser, J., *Acta crystallogr.*, 1961, **14**, 369.

⁴ Green, M., and Kirkpatrick, D., *J. chem. Soc. (A)*, 1968, 483.

with phenyl groups attached in the radial position. The point group symmetry of the molecule in the solid is $\bar{1}$ although close to $\bar{3}2/m$. With only a centre of symmetry there are three inequivalent arsenic sites in the lattice and therefore we expect and find three resonances.

Table 1. N.q.r. frequencies for arsenic ring compounds (1)–(4)



| Compound | <i>T</i> (K) | ν_Q (MHz) | Compound | <i>T</i> (K) | ν_Q (MHz) |
|----------|--------------|------------------------|------------------|--------------|----------------|
| (1) | 298 | 60·930, 62·680, 66·440 | (4) ^A | 298 | 78·081, 78·768 |
| (2) | 298 | 60·220, 67·884 | | 195 | 78·657, 79·350 |
| | 195 | 60·579, 68·402 | | 77 | 79·151, 79·772 |
| | 77 | 60·934, 68·873 | (4) ^B | 298 | 78·978 |
| (3) | 298 | 79·885, 80·65, 81·18 | | 195 | 79·708 |
| | 195 | 80·724 | | 77 | 80·330 |
| | 77 | 81·430 | (4) ^C | 298 | 78·449 |
| | | | | 195 | 79·178, 79·896 |
| | | | | 77 | 80·036, 80·494 |

^A As prepared by sublimation at 385 K and 10^{-2} Torr.

^B Recrystallized from benzene at 295 K.

^C Recrystallized from benzene at 295 K and pumped to remove benzene at 295 K.

The molecular unit of the pentafluorophenyl compound $(\text{AsC}_6\text{F}_5)_4$ was assumed to be a tetramer on the basis of its molecular weight and by analogy with the corresponding phosphorus compound $(\text{PC}_6\text{F}_5)_4$ whose crystal structure has recently been determined.⁵ The $(\text{PC}_6\text{F}_5)_4$ molecular unit is a four-membered ring of phosphorus atoms with pentafluorophenyl groups in the radial position, and possesses only a twofold symmetry axis (and thus two inequivalent phosphorus atoms), although it is close to the higher symmetry $\bar{4}2m$ of $(\text{PCF}_3)_4$ ⁶ and $(\text{AsCF}_3)_4$.⁷ Therefore the appearance of two resonances of approximately equal intensity in $(\text{AsC}_6\text{F}_5)_4$ is consistent with it being isostructural with $(\text{PC}_6\text{F}_5)_4$.

The structure of neither of the heterocyclic compounds has been determined.

The heterocyclic compound with the phenyl groups attached to the arsenic atoms possessed one moderately strong resonance at all temperatures, although at 298 K two weak resonances at 80·65 and 81·18 MHz were also detected. However, the principal structure appears to be one in which there exists a diad axis through the centre of the As–As and C=C bonds of the molecule.

⁵ Sanz, F., and Daly, J. J., *J. chem. Soc. (A)*, 1971, 1083.

⁶ Palenik, G., and Donohue, J., *Acta crystallogr.*, 1962, **15**, 564.

⁷ Mandel, N., and Donohue, J., *Acta crystallogr. (B)*, 1971, **27**, 476.

The analogous compound with pentafluorophenyl groups substituted for the phenyl groups appeared to exhibit at least three different structures depending on the method of purification:

(a) When initially purified by sublimation (385 K; 10^{-2} Torr) in finely powdered form, two resonances of approximately equal strength were observed, indicating possibly a differential rotation of each of the two C_6F_5 groups about their bonds to the As atoms.

(b) When crystallized from benzene at room temperature in long clear needles, a single resonance at a different frequency to the previous doublet was recorded, indicating a structure with a diad axis through the As-As and C=C bonds. High resolution n.m.r. spectra of a $CDCl_3$ solution of these crystals revealed the presence of benzene so that presumably this structure contains benzene of crystallization.

(c) After prolonged pumping (355 K; 10^{-2} Torr) the compound assumes a white flaky appearance and yields a single resonance at 298 K at a different frequency again. At 195 and 77 K two resonances are observed of approximately equal strength and this is interpreted as indicating a phase transition somewhere between 195 and 298 K. Recrystallization of this product from benzene yields the single line spectrum of stage (b) after which further pumping again yields the spectrum characteristic of stage (c).

The spectra recorded during stages (a), (b) and (c) of the purification process represent different structures and their existence would need to be borne in mind in an X-ray structure determination of this compound.