

NUCLEAR MAGNETIC RESONANCE STUDIES OF THE MOLECULAR STRUCTURES OF PHOSPHABENZENE AND ARSABENZENE PARTIALLY ORIENTED IN A NEMATIC SOLVENT

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(Received 23 November 1977)

ABSTRACT

The molecular structures of phosphabenzene and arsabenzene partially oriented in the nematic liquid crystal crystal EBBA were studied by NMR. The structures were in excellent agreement with the combined electron diffraction and microwave spectroscopic studies except the angle relating to the β hydrogens. Improved values for this parameter were suggested. The absolute signs of the J_{PH} of phosphabenzene and some information on the ^{31}P chemical shift anisotropies were also obtained.

INTRODUCTION

The molecular and electronic structure of group V congeners of pyridine [1—3] are of considerable interest because they should provide useful information for assessing the effect of the heteroatom on the bonding and aromaticity. Photoelectron [4], microwave [5—7], and electron diffraction [8—10] studies of several members of this series have been carried out. Recently a detailed NMR study of phosphabenzene, arsabenzene and stibabenzene in solution was completed [11]. The most interesting observations of the NMR investigation are that the α protons and carbons are highly deshielded, presumably due to the large diamagnetic anisotropies of the heteroatom, and that the phosphorus chemical shift in phosphabenzene also occurs at extremely low field. The magnetic ring current, often used as a gauge for aromaticity, was found to change in the direction of $\text{P} > \text{As} > \text{Sb}$.

Even though the combined electron diffraction (ED) and microwave spectroscopic (MW) analysis [8, 10] yielded complete structures for phosphabenzene and arsabenzene, the accuracy of the determination of the proton structure may still be less than desirable, because of the low sensitivity of both ED and MW for protons. This is reflected by the relatively large uncertainties for the parameters related to the hydrogen atoms, particularly the angles related to the β hydrogen. Often, as shown in ref. 7, the knowledge of the hydrogen structure will definitely help the analysis of the structure of the whole

molecule. Therefore we have studied the proton structure of these two molecules partially oriented in a liquid crystal solvent by NMR [12]. The results provide a comparison with the structure obtained by the combined ED and MW analysis.

We also studied the chemical shift of the phosphorus in phosphabenzene partially oriented in the liquid crystal phase. The chemical shifts of the partially oriented species provide some information on the anisotropy of the chemical shift tensor of the phosphorus nucleus.

EXPERIMENTAL AND SPECTRAL ANALYSIS

Phosphabenzene and arsabenzene were synthesized according to published procedures [1, 2]. Samples of phosphabenzene and arsabenzene were made up of ~ 5% (mole) and ~ 3% (mole) respectively in the nematic liquid crystal phase of *N*-(*p*-ethoxybenzylidene)-*p*-*n*'-butylaniline (EBBA). The liquid crystal solvent was thoroughly treated through several freeze-pump-thaw cycles before the solute was distilled in. The tubes were all sealed under vacuum, because both phosphabenzene and arsabenzene are air-sensitive. 5 mm NMR tubes were used for ^1H studies and 10 mm tubes for ^{31}P . All spectra were obtained on a Bruker HX-270 spectrometer, operating at 270 MHz for proton and at 109.2 MHz for ^{31}P spectra. About 25–50 transients were accumulated for each proton spectrum and 400 for the ^{31}P spectra. The probe temperature was about 25°C. For phosphabenzene, ^{31}P spectra were taken at several temperatures in an attempt to obtain spectra with different order parameters. A ^{31}P spectrum in the isotropic phase of EBBA at ~ 76°C was also recorded to give the isotropic chemical shift of ^{31}P in EBBA. Typical line widths in the nematic phase are 6–7 Hz for ^1H spectra and 8 Hz for ^{31}P spectra.

Spectra were analysed with the iterative program LEQUOR [13]. The rms errors for the spectral fit are 1.1 and 1.0 Hz respectively for the ^1H spectra of phosphabenzene and arsabenzene and about 1.7–2.2 Hz for the ^{31}P spectra. The parameters fitting to about 50 and 85 lines for the two proton spectra are given in Table 1. Dipolar couplings [12] and chemical shifts were also deduced from ^{31}P spectra where about 30–35 lines were assigned for each spectrum. Order parameters were then determined from the dipolar couplings using the structure determined for phosphabenzene from the proton spectrum.

Indirect spin–spin coupling constants, J_{ij} , were taken from the isotropic values of ref. 11. The isotropic J_{PH} were also measured in the isotropic phase of EBBA. The magnitudes were all within a fraction of a Hz of those reported in ref. 11. Subsequent structural analysis in the nematic phase also determines the absolute signs of the PH couplings.

TABLE 1

Spectral parameters from the PMR spectra of partially oriented phosphabenzene and arsabenzene (relative chemical shift in ppm, D_{ij} in Hz)^a

	Phosphabenzene	Arsabenzene
$D_{1,2}$	-40.13 ± 0.43^b	
$D_{1,3}$	-60.92 ± 0.43	
$D_{1,4}$	-60.79 ± 0.23	
$D_{2,3}$	-795.90 ± 0.20	-921.11 ± 0.44
$D_{2,4}$	-106.10 ± 0.25	-122.43 ± 0.45
$D_{2,5}$	-23.10 ± 0.14	-29.08 ± 0.22
$D_{2,6}$	-5.74 ± 0.36	-11.37 ± 0.36
$D_{3,4}$	-215.80 ± 0.30	-278.76 ± 0.36
$D_{3,5}$	-8.20 ± 0.38	-17.03 ± 0.42
$\nu_2 - \nu_4$	1.233 ± 0.003 (1.23) ^c	2.334 ± 0.004 (2.16) ^c
$\nu_3 - \nu_4$	0.165 ± 0.003 (0.34) ^c	0.127 ± 0.005 (0.31) ^c

^aAll J_{ij} taken from ref. 11. ^bErrors correspond to one standard deviation. ^cIsotropic values from ref. 11 in parentheses.

RESULTS AND DISCUSSION

A version of the iterative weighted least-squares program SHAPE [13], including vibrational correction [14] was used to fit the molecular geometry and a set of order parameters to the observed D_{ij} . The molecules have been shown by ED and MW studies to be planar and with C_{2v} symmetry. Therefore there are only two diagonal order parameters necessary to describe the orientation of the molecules. To set a reference distance, the distance H_2-H_6 was taken to be 4.720 Å for phosphabenzene and 4.836 Å for arsabenzene, which are the r_z values obtained from the combined ED and MW studies [8, 10].

Vibrational correction was performed in the same manner as described elsewhere [14, 15], where the contribution from harmonic vibration is subtracted and the resulting structural parameters correspond to the r_z structure [16]. The approximate harmonic force fields were constructed by transferring and extrapolating appropriate force constants from benzene [17] and pyridine [18], and were the same as those used in refs. 8 and 10. Mean square perpendicular and parallel amplitudes of vibration were calculated by using a normal coordinate program MSAV [19]. The force field and the mean square amplitudes of vibration are available from ASIS and BLLD [8, 10].

The order parameters and structural parameters derived from least squares optimization are given in Table 2, where the corresponding r_z structure determined from combined ED and MW studies are also listed for comparison. The order parameters showed that the molecules orient preferentially with the

TABLE 2

Proton coordinates and order parameters of phosphabenzene and arsabenzene derived from PMR spectra of partially oriented species (coordinates in Å, S is dimensionless)

	Phosphabenzene		Arsabenzene	
	NMR ^a	ED + MW ^b	NMR ^a	ED + MW ^c
x_1^d	0.0	0.0		
y_1	0.0	0.0		
x_2 ($-x_6$)	2.360 ^e	2.360 ± 0.014	2.418 ^e	2.418 ± 0.007
y_2 (y_6)	0.677 ± 0.013	0.679 ± 0.008	0.824 ^e	0.824 ± 0.006
x_3 ($-x_5$)	2.162 ± 0.013	2.173 ± 0.019	2.148 ± 0.014	2.154 ± 0.012
y_3 (y_5)	3.135 ± 0.007	3.053 ± 0.033	3.251 ± 0.017	3.224 ± 0.015
y_4	4.269 ± 0.022	4.271 ± 0.006	4.341 ± 0.040	4.364 ± 0.005
S_{yy}	0.0973 ± 0.0014		0.1112 ± 0.0019	
S_{xx}	0.00539 ± 0.00012		0.01118 ± 0.00017	
rms error	0.31 Hz		0.18 Hz	

^aThis work. ^bRef. 8. ^cRef. 10. ^dAll coordinates are r_z values. ^eValues assumed.

C_2 axis along the director of the liquid crystal. From the ratio of the order parameters, it can be shown that the ordering along the C_2 axis is much greater for these two molecules than that for pyridine [20, 21].

The agreements between the parameters derived from the present study and those from ED and MW methods are generally very good. For arsabenzene, all the difference in the proton coordinates determined from the two methods are well within the limit of two standard deviations. The largest discrepancy is in the coordinates of y_3 (and y_5). The direction of this difference and that of x_3 and x_5 indicates that the angle $C_\alpha C_\beta H_3$ might be larger than the ED and MW value of $117.4 \pm 2.1^\circ$ by about 1° . However this difference is certainly small compared with the experimental uncertainties of this parameter. Similarly for phosphabenzene, all coordinates except that of y_3 and y_5 are in excellent agreement. However the discrepancy of y_3 and y_5 from the ED and MW result are much larger than that in arsabenzene. Again, the $\sphericalangle C_\alpha C_\beta H_3$ of $114.8 \pm 4.8^\circ$ determined by ED and MW is probably too small. Increasing this angle by about $3-4^\circ$ will bring the result in good agreement with the present study. In their study of stibabenzene by microwave spectroscopy, Fong et al. [7] used an interesting parameter $\Delta\theta$, where $\Delta\theta = \sphericalangle C_\alpha C_\beta H_3 - \sphericalangle C_\gamma C_\beta H_3$, as an aid for choosing the most probable solution in their structural analysis. They observed that the value of $\Delta\theta$ for pyridine and a number of monosubstituted benzenes spans a rather narrow range of $0.1-1.2^\circ$. The ED and MW result for arsabenzene gives a small value of $\Delta\theta$ (-0.5°). But for phosphabenzene, $\Delta\theta = -6.8^\circ$, which is clearly much larger than $\Delta\theta$ for all the other molecules mentioned. Therefore, increasing $\sphericalangle C_\alpha C_\beta H_3$ by $\sim 1^\circ$ for arsabenzene and $3-4^\circ$ for phosphabenzene is apparently in the right direction. It is interesting to note that, with these changes, all the CH bonds in both phosphabenzene, arsabenzene and pyridine [22] do approximately bisect

the corresponding CCC angles. From the above analysis, it appears that no adjustment of the ring structure as determined by the combined ED and MW studies needs to be invoked to bring the two sets of results into full agreement. Small adjustments need to be made to fit the combined ED and MW data due to the change of the $C_\alpha C_\beta H_3$ angle. But they are expected to be small, and are readily discernable from the published covariance matrices resulting from these studies. The main change expected is in the angles PCH and AsCH respectively. The apparent discrepancy is understandable and reflects the complementary nature of these techniques. Both ED and MW are not very sensitive to hydrogen atoms, therefore the parameters relating to the hydrogen atoms, in this case particularly $\approx C_\alpha C_\beta H_3$, suffer relatively large errors. Also average CH bond lengths had to be used in the combined ED and MW studies. Therefore the proton structures derived by NMR in this study probably represent a more reliable result.

The structures of phosphabenzene and arsabenzene were also determined by fitting to the sets of D_{ij} without performing vibrational averaging. The disagreement between the NMR structure and the ED and MW studies are much larger than if vibrational averaging was included. This again demonstrates the necessity of vibrational averaging in molecular structure determination by NMR of partially oriented molecules.

In ref.11, the isotropic J_{PH} of phosphabenzene were reported. However only their magnitudes are obtainable from the isotropic spectrum. From the spectrum of partially oriented phosphabenzene, $2D_{PH} + J_{PH}$ can be measured. Therefore the isotropic values of the magnitude of J_{PH} were assumed. 2J (P—H) and 3J (P—H) for trivalent phosphorus are usually positive [23]. Indeed, absurd geometrical parameters as well as poor least squares fit resulted when either of these two spin—spin couplings was assumed negative. Similarly, if J_{14} , i.e. 4J (P—H), was assumed positive, poorer least squares fit and less reasonable geometrical result were obtained than if J_{14} was assumed negative. Therefore it is concluded from the present study that, for phosphabenzene, $J_{12} = 38$ Hz, $J_{13} = 8$ Hz and $J_{14} = -3.5$ Hz.

The chemical shift of ${}^{31}P$ in phosphabenzene was measured both in the isotropic phase at $\sim 76^\circ C$ and at several temperatures in the nematic phase of EBBA. The ${}^{31}P$ chemical shift in the isotropic phase of EBBA is at 208.6 ppm downfield from 85% H_3PO_4 . This value is very close to the value of 211 ppm in the isotropic solution of chloroform. The small difference may be due to a combination of temperature and solvent effect. In the nematic phase, however, σ is shifted upfield from the isotropic value by about 52—56 ppm for a range of temperatures, i.e., $\bar{\sigma}_{nem}$ is about 150 ppm downfield from 85% H_3PO_4 . Since phosphabenzene possesses C_{2v} symmetry, the difference in the chemical shifts between the isotropic and nematic phases can be expressed as

$$\bar{\sigma}_{nem} - \sigma_{iso} = \frac{2}{3} 5^{-1/2} C_{3z^2-r^2} [\sigma_{zz} - \frac{1}{2}(\sigma_{xx} + \sigma_{yy})] + (15)^{-1/2} C_{x^2-y^2} (\sigma_{xx} - \sigma_{yy})$$

where $\sigma_{iso} = 1/3 (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, σ_{ii} is the diagonal element of the shielding tensor and $C_{3z^2-r^2}$ and $C_{x^2-y^2}$ are Snyder's motional constants [24]. In

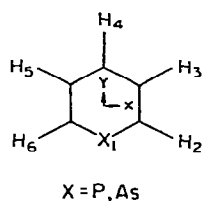


Fig. 1. Atomic numbering and axis system for phosphabenzene and arsabenzene.

principle, $\sigma_{zz} - 1/2 (\sigma_{xx} + \sigma_{yy})$ and $\sigma_{xx} - \sigma_{yy}$ can be measured with experiments with different $C_{x^2 - y^2} / C_{3z^2 - r^2}$ ratios [25]. The $\Delta\sigma$ value definitely indicates large chemical shift anisotropies. Our ^{31}P spectra taken at different sample temperatures did result in a range of varying $C_{x^2 - y^2} / C_{3z^2 - r^2}$ ratios. However, the resultant $\sigma_{zz} - 1/2 (\sigma_{xx} + \sigma_{yy})$ and $\sigma_{xx} - \sigma_{yy}$ from least squares are unreasonably large. We suspect that the anomalous result is due to the neglecting of the temperature dependence of the chemical shift, which has been reported previously, for example, for PH_3 [26]. Therefore, further work is required to eliminate the effect of temperature on the apparent chemical shift anisotropy before more reliable values of $\sigma_{zz} - 1/2 (\sigma_{xx} + \sigma_{yy})$ and $\sigma_{xx} - \sigma_{yy}$ can be obtained. The present experimental data, based on the measurement of σ_{iso} and $\bar{\sigma}_{\text{nem}}$ at approximately the nematic-isotropic transition temperature, provided the following equation

$$55.95 = 0.03226 [\sigma_{zz} - 1/2 (\sigma_{xx} + \sigma_{yy})] + 0.1909 (\sigma_{xx} - \sigma_{yy})$$

where the σ 's are expressed in ppm. Work is underway to study in more detail the ^{31}P chemical shift anisotropy, which is more informative on the electronic structure of the phosphorus atom than the averaged chemical shift.

ACKNOWLEDGEMENTS

We would like to thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and the Francis Bitter National Magnet Laboratory for use of the 270 MHz spectrometer.

REFERENCES

- 1 A. J. Ashe III, *J. Am. Chem. Soc.*, **93** (1971) 3293.
- 2 A. J. Ashe III, *J. Am. Chem. Soc.*, **93** (1971) 6690.
- 3 A. J. Ashe III and M. D. Gordon, *J. Am. Chem. Soc.*, **94** (1972) 7596; A. J. Ashe III, *Tetrahedron Lett.*, (1976) 415.
- 4 C. Batick, E. Heilbronner, V. Hornung, A. J. Ashe III, D. T. Clark, U. T. Cobley, D. Kilcast and I. Scanlan, *J. Am. Chem. Soc.*, **95** (1973) 928; J. A. Bastide, E. Heilbronner, J. P. Maier and A. J. Ashe III, *Tetrahedron Lett.*, (1976) 411; A. J. Ashe III, F. Burger, M. Y. El-Sheik, E. Heilbronner, J. P. Maier and J.-F. Muller, *Helv. Chim. Acta*, **59** (1976) 1944.

- 5 R. L. Kuczkowski and A. J. Ashe III, *J. Mol. Spectrosc.*, 42 (1972) 457.
- 6 R. P. Lattimer, R. L. Kuczkowski, A. J. Ashe III and A. L. Meinzer, *J. Mol. Spectrosc.*, 57 (1975) 428.
- 7 G. Fong, R. L. Kuczkowski and A. J. Ashe III, *J. Mol. Spectrosc.*, in press.
- 8 T. C. Wong and L. S. Bartell, *J. Chem. Phys.*, 61 (1974) 2840.
- 9 T. C. Wong, A. J. Ashe III and L. S. Bartell, *J. Mol. Struct.*, 25 (1975) 65.
- 10 T. C. Wong and L. S. Bartell, *J. Mol. Struct.*, 44 (1978) 169.
- 11 A. J. Ashe III, R. R. Sharp and J. W. Tolan, *J. Am. Chem. Soc.*, 98 (1976) 5451.
- 12 P. Diehl and C. L. Khetrupal, in *NMR—basic principles and progress*, Vol. I, Springer, Berlin, 1969.
- 13 P. Diehl, H. P. Kellerhals and W. Niederberger, *J. Magn. Reson.*, 4 (1971) 352.
- 14 P. Diehl and W. Niederberger, *J. Magn. Reson.*, 9 (1973) 495.
- 15 T. C. Wong and E. E. Burnell, *J. Mol. Struct.*, 33 (1976) 217.
- 16 Y. Morino, K. Kuchitsu and T. Oka, *J. Chem. Phys.*, 36 (1962) 1108; D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, 37 (1962) 1668.
- 17 S. J. Cyvin, *Molecular Vibration and Mean Square Amplitudes*, Elsevier, Amsterdam, 1968.
- 18 J. S. Struik and J. L. Walter, *Spectrochim. Acta Part A*, 27 (1971) 209.
- 19 R. L. Hilderbrandt and J. D. Wieser, *J. Chem. Phys.*, 56 (1972) 1143.
- 20 J. C. Robertson, C. T. Yim and D. F. R. Gilson, *Can. J. Chem.*, 49 (1971) 2345.
- 21 J. W. Emsley, J. C. Lindon and J. Tabony, *J. Chem. Soc. Faraday Trans. 2*, 71 (1975) 579
- 22 G. O. Sorensen, L. Mahler and N. Rastrup-Andersen, *J. Mol. Struct.*, 20 (1974) 119.
- 23 S. L. Manatt, G. L. Juvinall, R. I. Wagner and D. D. Elleman, *J. Am. Chem. Soc.*, 88 (1966) 2689; W. McFarlane, *Proc. R. Soc. Ser. A*, 306 (1968) 185.
- 24 L. C. Snyder, *J. Chem. Phys.*, 43 (1965) 4041.
- 25 G. J. den Otter, J. Bulthuis, C. A. de Lange and C. MacLean, *Chem. Phys. Lett.*, 45 (1977) 603.
- 26 N. Zumbulyadis and B. P. Dailey, *Mol. Phys.*, 27 (1974) 633.