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A ^{1}H and ^{31}P NMR Study of Phenylphosphonous Dichloride Partially Oriented in a Nematic Phase

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The ^{1}H and ^{31}P NMR spectra of phenylphosphonous dichloride dissolved in a nematic phase of *N*-(*p*-ethoxybenzylidene)-*p*-butylaniline (EBBA) have been analyzed, and the structure of the proton and phosphorus skeleton has been determined.

The NMR spectroscopy of molecules in the oriented phase has become a useful method of obtaining structural information about molecules since the first observation by Englert and Saupe.[1,2] In principle, the orientation parameters and the relative distances between the spin nuclei in a molecule can be determined by this technique.[3] The technique has been applied to many molecules containing various nuclei. However, only a few NMR studies have so far been reported on molecules containing the ^{31}P nucleus in the oriented phase.[3–7] This study will present the results of our own observation and analyses of the title substance dissolved in a nematic phase of *N*-(*p*-ethoxybenzylidene)-*p*-butylaniline (EBBA). The relative internuclear distances and the orientation parameters have been obtained.

Experimental

The phenylphosphonous dichloride (PPD) and EBBA were commercial in origin and were used without further purification.

The ^{1}H and ^{31}P NMR spectra of PPD in the isotropic phase were recorded at 60 and 24.28 MHz on a Hitachi R-20B spectrometer equipped with a R-204P attachment. In both cases, the spectra were obtained at 31.5±0.5 °C.

The ^{1}H and ^{31}P NMR spectra of PPD in an oriented phase were recorded on a Varian XL-200 spectrometer, operating both at 200 and 80.96 MHz for a 14.1 mol% solution in EBBA. Although there was a marked color change from colorless to yellow on the dissolving of PPD in EBBA, no chemical reaction occurred and the nematic solutions were stable for a week during the NMR measurements. The spectra were recorded with 32K data points using spectral widths of 20000 and 10000 Hz for the cases of ^{1}H and ^{31}P. Sixteen ^{1}H FIDs were accumulated without a lock for the proton spectrum, and 128 ^{31}P FIDs were accumulated with an external D_2O lock for the ^{31}P spectrum. In both cases, the sample was spun in the superconducting system. The probe temperature was about 22.5 °C. The average line-widths in the nematic phase were about 10 and 9 Hz for the ^{1}H and ^{31}P spectra respectively.

The calculation of the spectral and structural analyses were carried out by a HITAC E-600 minicomputer system installed in our laboratory.

Results and Discussion

Analyses of the Spectra. The ^{1}H NMR spectrum of PPD in the neat liquid consists of a large number of lines. Sixty-five lines were assigned. Analyses of the spectra were followed by a program, LAOCN3.[8] The results are given in Table 1. Sixty-five observed lines were assigned to the calculated values, with an RMS error of 0.08 Hz. The results were almost entirely consistent with those reported by Parr.[9] It was assumed that the phosphorus-proton couplings over three, four, and five bonds are positive. The numberings of the nuclei are shown in Fig. 1.

Table 1. ^{1}H NMR spectral parameters for phenylphosphonous dichloride in Hz

Isotropic phase[a]		Nematic phase[b]	
$J(1, 2)$	8.84 ± 0.02	$D(1, 2)$	-81.5 ± 0.7
$J(1, 3)$	1.91 ± 0.03	$D(1, 3)$	-46.0 ± 0.7
$J(1, 4)$	1.09 ± 0.05	$D(1, 4)$	-39.7 ± 0.3
$J(2, 3)$	7.66 ± 0.03	$D(2, 3)$	-1205.1 ± 0.2
$J(2, 4)$	1.13 ± 0.02	$D(2, 4)$	-148.1 ± 0.9
$J(2, 5)$	0.57 ± 0.02	$D(2, 5)$	8.0 ± 0.1
$J(2, 6)$	1.92 ± 0.02	$D(2, 6)$	91.8 ± 0.5
$J(3, 4)$	7.52 ± 0.02	$D(3, 4)$	62.9 ± 0.7
$J(3, 5)$	1.36 ± 0.02	$D(3, 5)$	93.0 ± 0.5
$\nu_2 - \nu_3$	28.23 ± 0.02	$\nu_2 - \nu_3$	49.5 ± 0.5
$\nu_2 - \nu_4$	25.62 ± 0.02	$\nu_2 - \nu_4$	-33.9 ± 0.5

a) Parameters obtained for the neat liquid. b) Parameters obtained for a 14.1 mol% solution in EBBA.

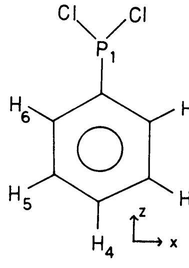

Fig. 1. Numbering system for phenylphosphonous dichloride.

The ^{1}H and ^{31}P NMR spectra of PPD in the nematic phase are given in Fig. 2. The spectra consisted of 55 and 18 resolved lines respectively. Eighty and 32 calculated lines were assigned for the observed ^{1}H and ^{31}P spectra, with an RMS error of 1.9 Hz. The results are also given in Table 1. The analyses of the spectra were followed by a program, LAOCN3D, which has been slightly modified from the LAOCN3+D program.[10] The indirect coupling constants were kept constant in the iteration calculation. The errors of the various parameters in Table 1 correspond to those given in the computer output.

The spectra calculated by varying the values of D_{12}, D_{13}, D_{26}, and D_{35}, while keeping $D_{12}+D_{13}$ and $D_{26}+D_{35}$ constant, were nearly identical. This means that only the sums ($D_{12}+D_{13}$ and $D_{26}+D_{35}$) can be determined with reasonable precision. When the difference between

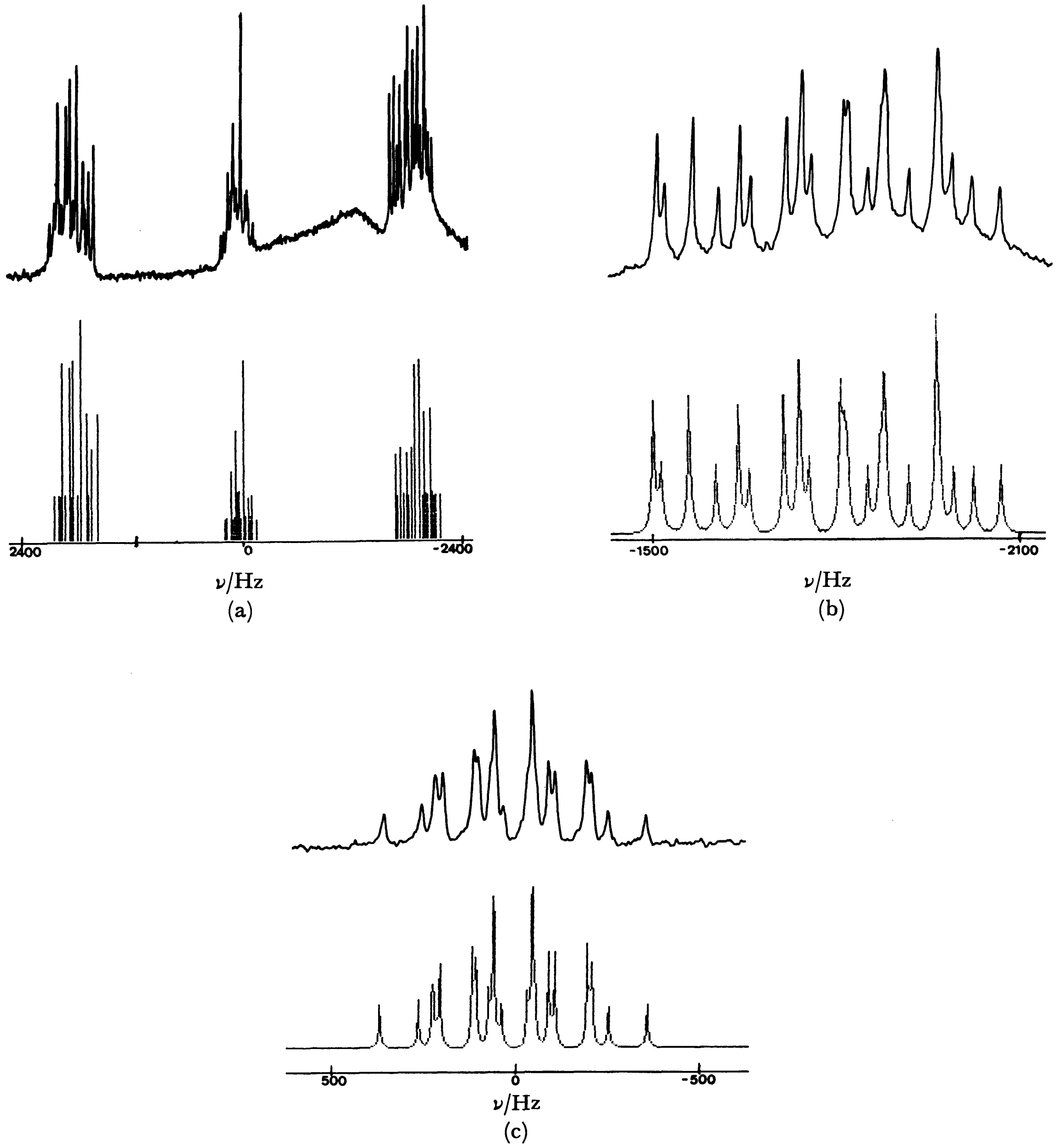

Fig. 2. Observed ^1H and ^{31}P NMR spectra of phenylphosphonous dichloride dissolved in EBBA. Calculated spectra are also given under the observed ones; (a) A whole observed ^1H spectrum accumulated 16 scans and a calculated stick spectrum, (b) an expanded upfield spectrum of (a) and a calculated one, (c) an observed ^{31}P spectrum accumulated 128 scans and a calculated one.

D_{26} and D_{35} is small, it is very difficult to differentiate D_{26} and D_{35} separately. However, a better agreement between the observed and the calculated spectra was obtained in the case of $D_{26}<D_{35}$.

Analyses of the Molecular Structure. PPD has been shown to be planar and to have a C_{2v} symmetry by means of an electron-diffraction study.[11] Therefore, there are only two diagonal-orientation parameters necessary to describe the molecular orientation. The three following assumptions were made before the analyses of the molecular structure: (1) the benzene ring forms a hexagonal plane; (2) molecular vibrations need not be taken into consideration; and (3) the anisotropies of the proton-phosphorus and proton-proton indirect couplings are negligible. Under these assumptions, the relative positions of the protons and the phosphorus can be determined from the direct proton-proton and proton-phosphorus couplings with the aid of the iterative program SHAPE.[12] The derived geometrical and orientation parameters are given in Table 2.

As may be seen in Table 2, the parameters derived from the present study agree with those from the electron-diffraction study within the limits of the standard deviation except in the case of the phosphorus atom. Two reasons for this discrepancy may be considered: (1) a vibration correction was not performed; or (2) the interatomic distances derived from NMR may deviate essentially from those of other methods.[3] The coordinates of the hydrogen atoms of PPD are in excellent agreement with those of phenylphosphonic

Table 2. COORDINATES OF THE SPIN NUCLEI IN PHENYLPHOSPHONOUS DICHLORIDE IN Å, AND ORDER PARAMETERS[a]

Nucleus	X Coordinate	Z Coordinate
P	0.0	5.874 ± 0.029
	(0.0)[b]	(5.74 ± 0.05)
H-2	2.182 ± 0.031	3.749 ± 0.054
	(2.16 ± 0.02)	(3.74 ± 0.02)
H-3	2.166 ± 0.031	1.249 ± 0.014
	(2.16 ± 0.02)	(1.25 ± 0.02)
H-4	0.0	0.0
H-5	−2.166 ± 0.031	1.249 ± 0.014
	(−2.16 ± 0.02)	(1.25 ± 0.02)
H-6	−2.182 ± 0.031	3.749 ± 0.054
	(−2.16 ± 0.02)	(3.74 ± 0.02)
S_{xx}	−0.06288 ± 0.00038	
S_{zz}	0.15689 ± 0.00013	

a) The calculated coordinates are based on the value of r(H-3, H-4), which is assumed to be 2.500 Å. b) The values in parentheses were calculated from the results obtained by means of the electron-diffraction method[11] (r(C–C) = 1.413±0.008, r(C–H) = 1.080±0.003, and r(C–P) = 1.833±0.04 Å).

dichloride.[7] However, as far as the coordinate of the phosphorus atom is concerned, the C–P distance of PPD is much longer than that of phenylphosphonic dichloride.[7] The above difference can, though, be partly explained by the fact that the C–P(III) (trivalent phosphorus) distance is slightly longer than the C–P(V) (pentavalent phosphorus) distance reported in electron-diffraction studies.[13,14]

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