April, 1992] © *1992 The Chemical Society of Japan* **NOTES** *Bull. Chem. Soc. Jpn.*, **65**, 1135—1137 (1992) 1135

Structure and Orientation of *o*-Phenylene Phosphorochloridite and *o*-Phenylene Phosphorochloridate Dissolved in a Nematic Phase

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Synopsis. The ^{1}H and ^{31}P NMR spectra of the title compounds dissolved in a nematic phase of *N*-(*p*-ethoxybenzylidene)-*p*-butylaniline (EBBA) were analyzed, and the structures of the proton and phosphorus skeleton determined.

Several NMR studies have so far been reported concerning molecules containing the ^{31}P nucleus in the oriented phase.[1–9]

This study presents the results of our own observations and analyses of the title substances dissolved in a nematic phase of *N*-(*p*-ethoxybenzylidene)-*p*-butylaniline (EBBA).

Experimental

o-Phenylene phosphorochloridite and chloridate (hereafter referred as **1** and **2**) as well as EBBA were commercial in origin and used without further purification.

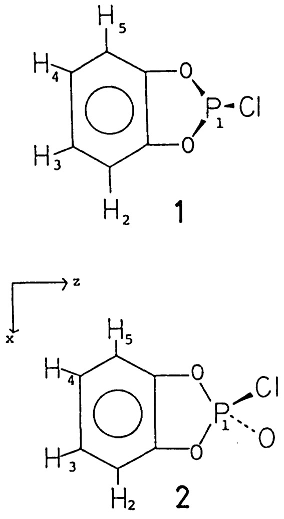
The ^{1}H and ^{31}P NMR spectra in an isotropic solution were observed at 60 and 24.28 MHz on a Hitachi R-20B spectrometer in $CDCl_3$. The sample concentrations in the nematic solutions were about 13.1 and 14.3 mol% for **1** and **2**, respectively. The ^{1}H and ^{31}P NMR spectra of **1** and **2** in the nematic solutions were recorded on a Varian XL-200 spectrometer, operating at both 200 and 80.96 MHz at about 24 °C. The average line-widths in the nematic solutions were about 14 and 16 Hz for the ^{1}H and ^{31}P spectra, respectively.

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

Results and Discussion

Analyses of the Spectra. The ^{1}H NMR spectrum of **1** in a $CDCl_3$ solution was analyzed as an AA′BB′X spin system by using a program called LAOCN3.[10] The numberings of the magnetic nuclei in the molecules are given in Fig. 1. Fifteen observed lines were assigned to fifty calculated lines with an RMS error of 0.13 Hz. The results are given in Table 1, which are almost consistent with the reported values.[11] The proton–phosphorus coupling constants of **1** and **2** have not been reported yet. They have therefore been assumed to be positive, following a reported reference.[12] The obtained values are small, due to the distance between two nuclei through four or five bonds apart. The ^{31}P NMR spectra of **1** and **2**, as well as the ^{1}H NMR spectra of **2** in isotropic solutions were observed as a single line, and could not be resolved. This different appearance of the ^{1}H NMR spectra of **1** and **2** was estimated to be due to the presence or absence of a small chemical-shift difference of two protons of **1** or **2**.

The ^{1}H and ^{31}P NMR spectra observed in the nematic solutions were analyzed using a program called LAOCN3D.[9] The ^{31}P and ^{1}H NMR spectra of both **1** and **2** were similar in appearance, and consisted of 7 and



1

2

Fig. 1. Numbering systems for **1** and **2**.

Table 1. Spectral Parameters for **1** and **2** in Hz

1				2	
Isotropic phase[a)]		Nematic phase[b)]		Nematic phase[b)]	
$J(1,2)$	0.59±0.08	$D(1,2)$	−46.8±0.6	$D(1,2)$	−55.3±0.4
$J(1,3)$	0.19±0.08	$D(1,3)$	−33.8±0.6	$D(1,3)$	−41.2±0.4
$J(2,3)$	7.87±0.04	$D(2,3)$	−685.4±0.3	$D(2,3)$	−827.5±0.2
$J(2,4)$	1.18±0.03	$D(2,4)$	−8.1±0.3	$D(2,4)$	3.8±0.2
$J(2,5)$	0.56±0.08	$D(2,5)$	37.1±0.7	$D(2,5)$	55.8±0.5
$J(3,4)$	7.59±0.08	$D(3,4)$	304.2±0.8	$D(3,4)$	470.5±0.5
ν_3	423.77±0.04	$\nu_3-\nu_2$	−1.5±0.9	$\nu_3-\nu_2$	19.3±0.6
ν_2	431.89±0.04				

a) Measured at 60 MHz. b) Measured at 200 MHz.

24 lines, respectively. Therefore, analyses of the spectra of both **1** and **2** in nematic solutions were carried out using the same indirect couplings as those given in Table 1. Thus, 16 and 26 calculated lines were assigned for the observed ^{1}H spectra of **1** and **2** with RMS errors of 2.2 and 1.7 Hz, respectively. The results for nematic solutions are also given in Table 1. The errors of the various parameters given in Table 1 correspond to those given in the computer output. The ^{1}H and ^{31}P NMR spectra of **1** are given in Figs. 2 and 3 as typical examples.

Analyses of the Molecular Structures. The structures of **1** and **2** were studied by an electron diffraction (ED) method, as described previously.[13,14] Although the heavy-atom moieties of **1** and **2** in the hetero-ring have been known by an ED study, the inter-proton distances have not yet been reported. Both **1** and **2** have C_s symmetry. However, four protons sit on a plane. Therefore, as far as the proton skeletons are concerned, two molecules can be analyzed in a similar manner. The direct couplings given in Table 1 were used to determine geometrical information concerning the molecules. The relations between the ratios of the inter-proton distances and the direct couplings are given according to the three following equations:[15]

$$(R_{34}/R_{25})=(D_{25}/D_{34})^{1/3},$$

$$D_{23}(R_{23}/R_{25})^5-D_{24}[(D_{25}/D_{34})^{1/3}+(R_{23}/R_{25})^2]^{5/2}=-D_{25}(D_{25}/D_{34})^{1/3},$$

and

$$(R_{24}/R_{25})^2=(D_{25}/D_{34})^{1/3}+(R_{23}/R_{25})^2.$$

The orientation parameters (S_{xx} and S_{zz}) are related to the D's and R's according to the two following equations:[15]

$$S_{xx}=-(4\pi^2/h\gamma^2)D_{25}R_{25}^3$$

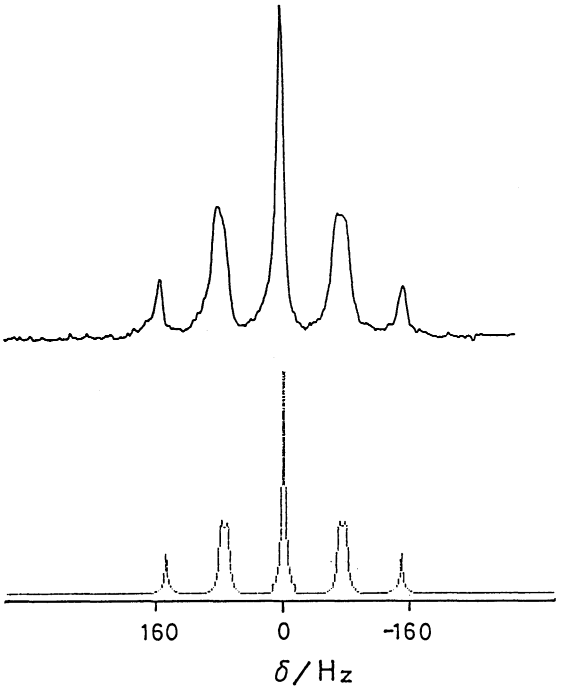


Fig. 2. Observed(upper) and calculated(lower) ^{31}P NMR spectra of **1** dissolved in EBBA at 80.96 MHz and 24 °C.

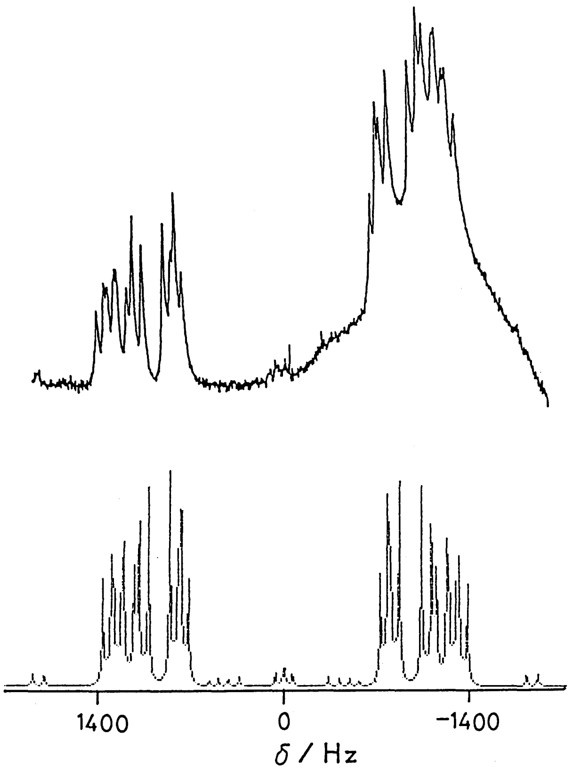


Fig. 3. Observed (upper) and calculated (lower) ^{1}H NMR spectra of **1** dissoloved in EBBA at 200 MHz and 24 °C.

Table 2. Geometrical and Order Parameters for **1** and **2**

Parameter	**1**(A)	**1**(B)	**2**
R_{12}/R_{34}	1.718±0.023 (1.744)[a)]	1.679±0.032	1.726±0.017 (1.751)
R_{13}/R_{34}	2.317±0.025 (2.344)	2.275±0.034	2.320±0.019 (2.357)
R_{23}/R_{34}	1.019±0.006 (1.000)	1.017±0.005	1.016±0.004 (1.000)
R_{24}/R_{34}	1.753±0.007 (1.731)	1.746±0.006	1.753±0.005 (1.731)
R_{25}/R_{34}	2.034±0.018 (2.000)	2.015±0.016	2.040±0.012 (2.000)
S_{xx}	−0.03868±0.00011	−0.03868±0.00011	−0.05982±0.00011
S_{zz}	0.13757±0.00311	0.13495±0.00262	0.17084±0.00251
S_{yz}		−0.00150±0.01331	

a) The values in parentheses were calculated from the parameters obtained by means of the electron-diffraction method.

and

$$S_{zz}=-(4\pi^2/h\gamma^2)R_{23}^3\times[D_{23}-(D_{25}/4)(R_{23}/R_{25})^{-5}((D_{25}/D_{34})^{1/3}-1)^2]\times[1-(1/4)(R_{23}/R_{25})^{-2}((D_{25}/D_{34})^{1/3}-1)^2]^{-1}.$$

The inter-proton distances and orientation parameters concerning the four protons were obtained from the data given in Table 1 with the aid of an iterative program called SHAPE.[16] The results are given in Table 2, where R_{34} is assumed to be 2.481 Å in both samples. After the inter-proton distances were determined, the phosphorus coordinates could be obtained by using the values of D_{12} and D_{13}. An ED study tells us that the phosphorus atom of the **2** sits on a molecular plane formed with six carbons and two oxygens, but that of **1** does not.[13,14] Otherwise, for **2**, the Cl–P–O plane is perpendicular to the molecular plane.[14] Therefore, it is easy to obtain the phosphorus coordinates for **2**, since there are two D's for obtaining two coordinates of the phosphorus atom. For **1**, however, two D's are not sufficient to determine the phosphorus coordinates. An additional assumption is thus necessary. The following two cases (A and B) were considered in order to obtain the coordinates:

A) The five-membered hetero-ring is planar.
B) The five-membered hetero-ring is not planar.

In case A, the situation concerning a structural analysis of **1** is similar to that of **2**. An analysis can thus be easily made. In case B, however, the coordinates are in an "underdetermined" condition. Therefore, one parameter among three (S_{yz}, z-, and y-coordinates of the phosphorus atom) is fixed to a given value; the two remaining parameters are thus iterated with the aid of a program (SHAPE) in order to obtain the most suitable structure from the observed D_{12} and D_{13}. The fixed value of one of the given parameters is thus changed to another given value; this procedure is continued until the error in the program (SHAPE) reaches a minimum error between the observed and calculated values of the D's. This technique was used before.[6] The results are given in Table 2.

From Table 2, the values of R_{12} are shown to be shorter than those calculated from the electron diffraction studies by about 1.5% in length, as given in parentheses. The values of R_{23}, R_{24}, and R_{25}, however, are larger than those calculated for the symmetrical hexagone of benzene(their ratios are 1.000, 1.732, and 2.000). The reason for this is considered to be as follows. The C–H bond near an electronegative atom, such as oxygen, can be polarized to the form C^{-}–H^{+}. Therefore, the hydrogen is attracted by an electrostatic force to a neighboring oxygen atom in the molecule. This effect can explain the longer inter-proton distances of these molecules. This tendency was also pointed out regarding benzo[*b*]furan,[17] quinoxaline,[18] and phthalazine.[19]

The R_{12} and R_{13} of **1** (case A) are longer than those of **1** (case B). This may be reasonable based on the above-mentioned assumption.

The orientation parameters of **1** and **2** are similar in magnitude. S_{zz} is larger than S_{xx}, and even S_{yz} is nearly zero. The positive S_{zz} of **1** and **2** indicate that their preferred orientations are along the z-axis with the magnetic field direction.

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