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^{13}C Spin-lattice Relaxation and Molecular Structure. II.[1] The Application of ^{13}C Spin-lattice Relaxation Times (T_1) to Assignments of Signals in the Proton-decoupled ^{13}C NMR Spectrum of 5-Ethyl-5*H*-dibenzophosphole

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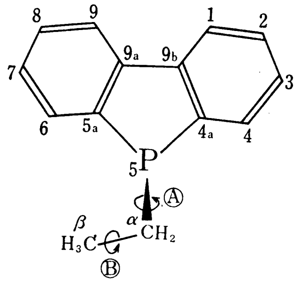
The spin-lattice relaxation times (T_1) of the ^{13}C nuclei in 5-ethyl-5*H*-dibenzophosphole (**1**) were studied. The ^{13}C NMR signals of the quaternary carbons of **1** in the aromatic region, whose assignments are very difficult by other techniques, were successfully assigned by means of the spin-lattice relaxation method. The dipolar relaxation terms and their reciprocal values were calculated by the use of the internuclear-distances between the carbon nuclei and hydrogen or phosphorus ones, and were compared with the observed T_1 values. It was found by studying the observed T_1's of the ethyl group in **1** that the rotation around the C–P bond is more strongly restricted than that around the C–C single bond.

As the recent development of the FT method in NMR spectroscopy has facilitated the measurement of ^{13}C spin-lattice relaxation times (T_1), the application of the T_1 method to the study of molecular geometries and motions is a recently developing field.[1–3] Moreover, the T_1 method has become a useful method for the assignment of signals in the ^1H-decoupled ^{13}C NMR spectra of various organic molecules.[4]

In the study of the catalytic hydroformylation of olefins by rhodium- or cobalt-tertiary phosphine complexes, dibenzophospholyl derivatives have been revealed to be efficient catalyst ligands.[5] In the course of the spectroscopic elucidation of the effectiveness of the catalysts, it was necessary to assign the ^{13}C NMR signals of the dibenzophospholes.[5] Moreover, the signal assignments of ring carbons are important for the study of the aromaticity of phospholes.[6] However, it is very difficult to assign the signals of quaternary carbons in dibenzophospholes by techniques such as those employing the chemical shifts and the coupling patterns of J_{CH} in the ^1H-undecoupled ^{13}C spectrum. In addition, the coupling constants between the carbon and phosphorus nuclei (J_{CP}) cannot give us fully conclusive information about the signal assignments, as will be described later. In the view of these factors, the spin-lattice relaxation method is expected to be useful to overcome the difficulty.



In this report, we will describe the first application of the T_1 method to the ^{13}C NMR signal assignments of a tertiary phosphine, choosing 5-ethyl-5*H*-dibenzophosphole (**1**) as an example. The internal rotation of the ethyl group of **1** will also be discussed briefly.

Experimental

Materials. The 5-ethyl-5*H*-dibenzophosphole (**1**) and ethyldiphenylphosphine (**2**) were prepared according to a procedure similar to that used for 5-benzyl-5*H*-dibenzophosphole[7] in a pure nitrogen atmosphere. **1** and **2** were NMR spectroscopically pure.

Spectral Measurements. The ^{13}C NMR spectra were recorded on a NEVA NV-14 spectrometer operating at 15.087 MHz with a Varian 620/L computer (16 K) for a pulse FT method. The T_1's were determined by the usual 180°-τ-90° pulse-sequence method. The pulse-delay time was set at five times greater than the longest T_1 to be measured. Free induction decays were accumulated for from 40 to 400 times. The spectral width was 1000 Hz for the aromatic carbon signals and 600 Hz for the alkyl carbon signals. In order to avoid the oxidation of the phosphine and the influence of the dissolved oxygen on the T_1 value of each nucleus, the sample containing degassed 20 vol% of acetone-d_6 was sealed under pure nitrogen. The T_1 values were evaluated by means of the least-squares method, using from 6 to 8 data points. The errors of the T_1 values thus obtained are smaller than *ca.* 10%.

Results and Discussion

The ^1H-decoupled ^{13}C spectrum of **1** is shown in Fig. 1. The peaks are alphabetically labelled from the lowest field as is shown in Fig. 1. Although **1** has eight kinds of carbons, the ^1H-decoupled ^{13}C spectrum consists of fourteen peaks due to various couplings (J_{CP}) between carbon-13 and phosphorus nuclei. The usual and easiest way to assign these signals is to obtain the information by investigating the coupling constants, J_{CH} in a ^1H- and ^{31}P-undecoupled ^{13}C spectrum or J_{CP} in a ^1H-decoupled ^{31}P-undecoupled ^{13}C spectrum. In the former technique, however, full information cannot be obtained because of the considerable overlapping of peaks in the aromatic region,* although in the alkyl region, the higher-field peaks of M and N can be assigned to the methyl carbon based on their coupling patterns. On the other hand, in the latter technique, it was expected that the assignment might be made by

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* It can only be said that the A—D peaks are assigned to quaternary carbons at the 4a(5a) and 9a(9b) positions.

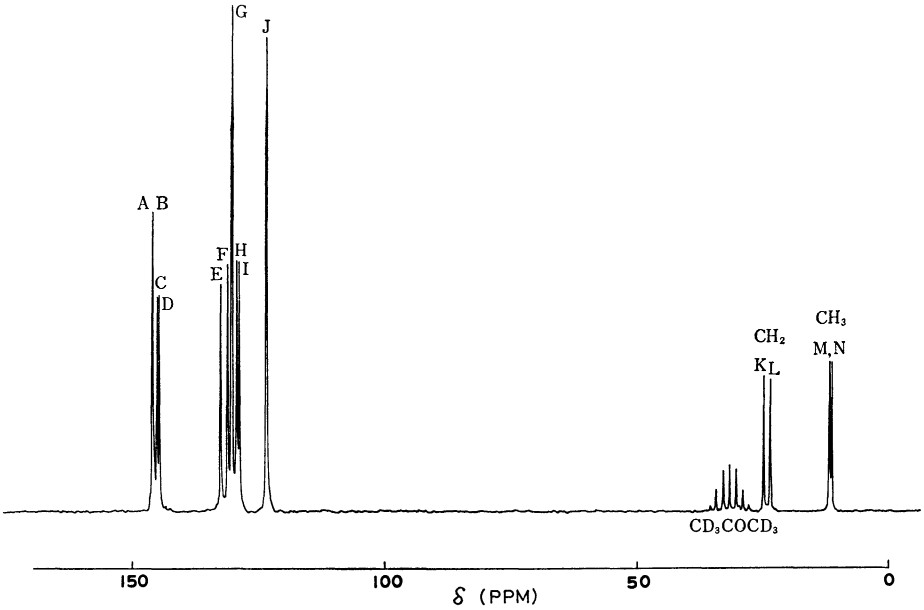

Fig. 1. The ^{1}H decoupled ^{31}P undecoupled ^{13}C NMR spectrum of **1** (at 15.087 MHz, spectrum width: 3300 Hz, pulse width: 35 μs, pulse delay: 25 s, accumulation: 3200 times, sensitivity enhancement: 0.2 s, ^{2}D lock).

considering the differences in the values of the coupling constants between the phosphorus and carbon nuclei at the α, β, γ, and δ positions. Unfortunately, however, the coupling constant between α-carbon and the phosphorus nuclei ($^{\alpha}J_{\rm CP}$) is not always larger than that between β-carbon and the phosphorus nuclei ($^{\beta}J_{\rm CP}$).[8,9] In addition, it was found that the order in the coupling constants of methylene and methyl carbons ($^{\alpha}J_{\rm CP}$ and $^{\beta}J_{\rm CP}$) is reversed in **1** and in ethyldiphenylphosphine (**2**), as is shown in Table 1. Therefore, the straightforward assignment of, for example, quarternary carbons at 4a(5a) and 9a(9b) cannot be made from the $J_{\rm CP}$ coupling constants.

TABLE 1. THE COUPLING CONSTANTS[a)] BETWEEN THE PHOSPHORUS AND α- AND β-CARBON NUCLEI OF THE ETHYL GROUP IN **1** AND **2**

Compound	$\frac{^{\alpha}J_{\rm CP}(\rm CH_2)}{\rm Hz}$	$\frac{^{\beta}J_{\rm CP}(\rm CH_3)}{\rm Hz}$
1	19.0	6.6
2[b)]	10.9	16.9

a) The signs of these coupling constants are not taken into account. b) The values reported in Ref. 8 are the reverse of our data. Probably, the literature data is somehow a mistake.

The third method for the assignment is the comparison of chemical shifts of **1** with those of structurally analogous compounds, for example, **2**. Since the five-membered ring in **1** is strained because of the deviations of the bond angles at the sp^2 carbon and phosphorus atoms from 120 and 109.5° respectively, and since the aromaticity[6)] in the ring of **1** may make the situation more complex, the chemical shifts of C(4a), C(5a), C(9a), and C(9b) in **1** cannot be directly compared with those in **2**.

Therefore, the spin-lattice relaxation method was employed to overcome these difficulties, since T_1 is a quantity closely related to molecular structures and motions.

As the ^{13}C NMR spectrum of **1** in this study is a ^{1}H-decoupled and ^{31}P-undecoupled ^{13}C spectrum, its spin system contains spin-spin couplings ($J_{\rm CP}$). It is generally considered[10—16)] that the T_1's in such a spin system with spin-spin coupling as **1** are complex and different from those in a spin system without spin-spin couplings, because the presence of cross-correlation phenomena between the coupling nuclei may influence the T_1 values. For example, the longitudinal components (T_1 components) of the magnetic moments in the former spin system do not show simple exponential decays by a dipole-dipole relaxation mechanism, whereas in the latter spin system (*e.g.*, in a ^{1}H- and ^{31}P-decoupled ^{13}C spectrum of **1**) they show simple exponential decays. In our case, however, the cross-correlation is expected to be negligibly small because of the extremely remote resonances of carbon-13 and the phosphorus nuclei: $|J_{\rm CP}|/(\omega_{\rm P}-\omega_{\rm C})\ll 1$, ($|J_{\rm CP}|\leqq 21.3$ Hz, and $\omega_{\rm P}-\omega_{\rm C}=9.2$ MHz at 15.1 MHz for ^{13}C nuclei). If this is not the case, the decay curves of the longitudinal components of the magnetic moments in the ^{13}C nuclei of **1** cannot be described by a single exponential decay.[11)] Actually, the experimentally obtained decay curves unambiguously show straight lines in all peaks of **1**. The decay curves of Peaks A—D are shown in Fig. 2 as examples. Moreover, if the cross-correlation effect is large, the T_1 value of one peak in the doublet signal in **1** must be different from that of the other peak.[10—11)] However, the obtained "apparent" T_1 value** of one peak in the doublet is almost the same as that of the other counterpeak, within the limits of experimental error, as is

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** T_1 values which are evaluated by means of the usual method used for a decoupled spin system.

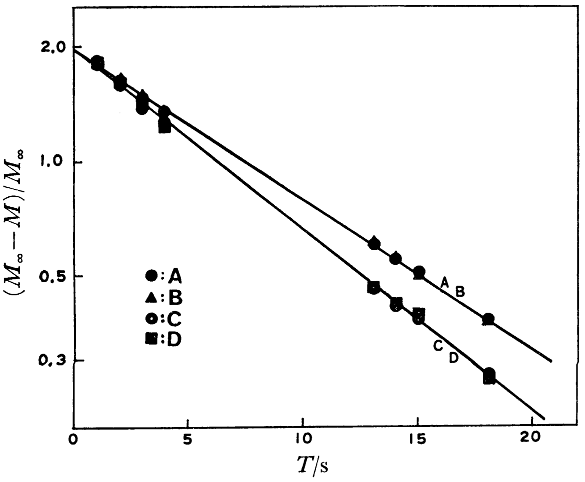

Fig. 2. The semi-log plot of $(M_\infty - M)/M_\infty$ versus pulse delay time (T) of the peaks A—D in the ^{1}H decoupled ^{31}P undecoupled ^{13}C NMR spectrum of **1**.

Table 2. The chemical shifts (δ, from TMS internal), coupling constants ($|J_{CP}|$), T_1 values, and assignments of the peaks in **1**

Peak	$\frac{\delta}{\text{ppm}}$	$\frac{\lvert J_{CP}\rvert}{\text{Hz}}$	$\frac{T_1}{\text{s}}$	Carbon
A B	144.7	1.5	10.9 11.3	9a, 9b
C D	143.6	6.7	9.3 9.2	4a, 5a
E F	130.6	21.3	0.45 0.44	
G	129.1	0	0.41	
H I	127.9	7.4	0.40 0.39	
J	122.1	0	0.44	
K L	22.5	19.0	0.56 0.49	α(CH$_2$)
M N	9.5	6.6	1.8 1.9	β(CH$_3$)

shown in Table 2. Thus, these results indicate that, in the case of **1**, the "true" T_1 values should be almost the same as the "apparent" T_1 values of the doublet peaks of the carbon-13 signals. From now on, for convenience, in this paper we will refer to the "apparent" T_1 values as T_1 values.

Although ^{13}C nuclei can be relaxed by four mechanisms (dipole-dipole, spin-rotation, chemical shift anisotropy, and scalar mechanisms), the latter three mechanisms can be excluded in the case of **1**, because **1** is a considerably large molecule and the obtained T_1's are relatively small (<12 s). The T_1 by the dipole-dipole mechanism is described as the following equation:

$$\frac{1}{T_1^{\mathrm{dd}}} = \hbar^2 \gamma_{\mathrm{C}}^2 \left\{ \gamma_{\mathrm{H}}^2 \sum_i \frac{N_i}{r_i(\mathrm{CH})^6} + \gamma_{\mathrm{P}}^2 \frac{1}{r(\mathrm{CP})^6} \right\} \tau_{\mathrm{c}}, \tag{1}$$

where γ_{C}, γ_{H}, and γ_{P} are the gyromagnetic ratio of carbon-13, hydrogen, and phosphorus respectively, N is the number of equivalent nuclei, r is the internuclear distance, and τ_{c} is the correlation time. It can be assumed, considering the molecular shape, that an isotropic (or pseudoisotropic) overall tumbling motion occurs in **1**. Thus, the common correlation time τ_{c}, may be adopted for carbons in the dibenzophospholyl moiety, but for the ethyl carbons the τ_{c}'s by both the tumbling motion and the internal rotation must be considered.

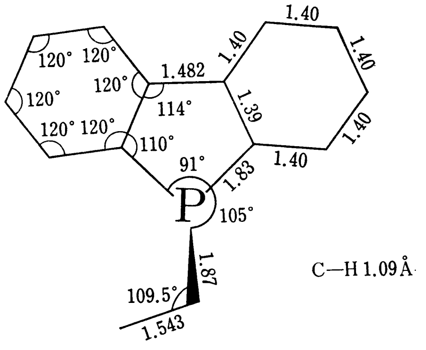

Fig. 3. The assumed bond lengths and bond angles of **1**.

The molecular geometry of **1** was assumed to be as is shown in Fig. 3. The bond lengths and bond angles described in Fig. 3 were assumed by analogy with ethane, benzene, triphenylphosphine,[17)] benzylphosphole,[18)] and a metal complex of **1**.[19)] According to Eq. 1, the value of the dipolar term, $[\sum_j \hbar^2 \gamma_{\mathrm{C}}^2 \gamma_{\mathrm{X}(j)}^2 (\sum_i N_i/r_i^6)]$ (X(j): nuclei which relax the carbon-13 nucleus), and its reciprocal, $[T_1 \cdot \tau_{\mathrm{c}}]$, were calculated*** using the internuclear-distances, r_{CH} and r_{CP}, evaluated from these data. The results are shown in Table 3.

Table 3. The calculated dipolar terms[a)] and their reciprocal ($T_1 \cdot \tau_{\mathrm{c}}$) values of the carbons in **1**

Carbon	$\frac{\text{Dipolar term}}{10^{10}\ \mathrm{s}^{-2}}$	$\frac{T_1 \cdot \tau_{\mathrm{c}}}{10^{-11}\ \mathrm{s}^2}$
1, 9	2.18	4.59
2, 8	2.22	4.50
3, 7	2.22	4.50
4, 6	2.19	4.57
4a, 5a	0.0568	176
9a, 9b	0.0428	234
α(CH$_2$)	4.41	2.27
β(CH$_3$)	6.51	1.54

a) $\equiv \sum_j \hbar^2 \gamma_{\mathrm{C}}^2 \gamma_{\mathrm{X}(j)}^2 \left(\sum_i \frac{N_i}{r_i^6} \right)$.

Quarternary Carbons. C(4a) mainly relaxes by one β-hydrogen, four γ-hydrogen, and one α-phosphorus nuclei, while C(9a) mainly relaxes by one β-hydrogen, three γ-hydrogen, and one β-phosphorus nuclei. The calculations show that the contribution to the relaxation by δ-positioned nuclei is negligibly small. The differences in the number and position of the counter-atoms for relaxation cause the deviation of the dipole-dipole relaxation times of the carbons with a common tumbling

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*** The deviation of the assumed bond-length from the real one is expected to be not more than the amount whose contribution is estimated to be less than 5% of the $T_1 \cdot \tau_{\mathrm{c}}$ value, judging from the X-ray analylsis data of triphenylphosphine,[17)] benzylphosphole,[18)] and the metal complex of **1**.[19)] motion. The observed T_1 values of Peaks A—D are much greater than those of Peaks E—J. This indicates that Peaks A—D must be assigned to the quaternary carbons, 4a(5a) and 9a(9b). In comparison with the observed T_1 and calculated $T_1 \cdot \tau_c$ values (see Tables 2 and 3), Peaks A and B are assigned to carbons 9a and 9b, and Peaks C and D, to carbons 4a and 5a. The observed T_1 ratio between C(9a) and C(4a) is in excellent agreement with the calculated T_1 ratio: $T_1(9a)^{\mathrm{obsd}}/T_1(4a)^{\mathrm{obsd}}=1.2$ and $T_1(9a)^{\mathrm{calcd}}/T_1(4a)^{\mathrm{calcd}}=1.3$. This means that the few assumptions made in this investigation are sufficiently valid.

Aromatic CH Carbons. All the calculated $T_1 \cdot \tau_c$ values of aromatic CH carbons are almost the same. Although the numbers and positions of the counter-atoms for the relaxation are different from each other in the aromatic CH carbons, the contribution to the relaxation by the α-hydrogen nuclei is overwhelmingly large. The observed T_1 values are almost the same, within the limits of experimental error (0.39—0.45 s). The equality in the observed T_1's of four kinds of aromatic CH carbons and the same calculated $T_1 \cdot \tau_c$ values indicate that all these carbons have a common correlation time, τ_c; an isotropic tumbling motion occurs in **1**. Therefore, we cannot obtain any information about the assignment of the aromatic CH carbons in **1** by means of the T_1 technique.

Ethyl Carbons. As has been described before, Peaks K and L were assigned to the methylene carbon, and Peaks M and N, to the methyl carbon, judging from their coupling patterns in ^{1}H-undecoupled ^{13}C spectrum. As the methylene carbon is bonded to two hydrogen (H) atoms and one phosphorus atom as the counter-atoms for the dipolar relaxation, and the methyl carbon, to three H atoms, the T_1's of these carbons may be expected to be different from each other. The calculated $T_1 \cdot \tau_c$ values are 2.27×10^{-11} s^2 for CH$_2$ and 1.54×10^{-11} s^2 for CH$_3$. However, the observed T_1's are the opposite; 0.53 s for CH$_2$ and 1.8 s for CH$_3$. The results indicate that the correlation times (τ_c) of the methylene and methyl carbons are quite different from each other, and the observed T_1's show that the rate of the internal rotation of the methyl group (B) is much faster than that of the internal rotation of the ethyl group (A) (*cf.* Eq. 1). This is an unexpected result, for the rotation around the C(sp^3)–C(sp^3) bond is known to be more strongly restricted than that around the C–P bond. For example, it is known from microwave spectroscopy that the rotational barrier around the C–C bond in isobutane is higher than that around the C–P bond in trimethylphosphine,(20) and that the barrier in ethane(21) is higher than that in methylphosphine,(22) as is shown below: V/(kcal/mol); $(CH_3)_3CH$: 3.9,(20) $(CH_3)_3P$: 2.6,(20) CH_3-CH_3: 3.0,(21) and CH_3PH_2: 1.96.(22) This interesting fact, that the A roration in **1** is more strongly restricted than the B rotation, may be explained by considering that the substituent at the phosphorus atom (*i.e.*, the *o,o'*-biphenylene group) is much bulkier than that at the β-carbon atom (*i.e.*, three hydrogen atoms); this steric repulsion effect may mainly raise the barrier to rotation around this C–P bond, although the bond-length (1.87 Å) between C_α and P atoms is considerably longer than that (1.54 Å) between C_α and C_β atoms.

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