Demonstrations of NMR Quantum Information Processing Utilizing ^{31}P Nuclei of Phosphorus Heterocycles

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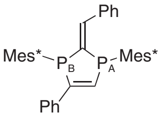
^{31}P NMR data of a 1,4-diphosphafulvene (alkylidene-2,3-dihydro-1*H*-1,3-diphosphole) and a 3,4-dihydro-1,3,4-triphosphacyclopenta[*a*]indene, bearing two or three chemically inequivalent phosphorus nuclei, were promising to be applicable for solution ^{31}P NMR quantum information processing, and demonstrations including implementation of the Deutsch–Jozsa algorithm with ^{31}P nuclei were examined.

Phosphorus heterocycles containing π-conjugated molecular skeletons have widely been employed for exploration of novel materials.[1] 1,4-Diphosphafulvene **1**[2] and 3,4-dihydro-1,3,4-triphosphacyclopenta[*a*]indene **2**[3] contain unique π-extended diphosphole-type skeletons, and several properties concerning electron-transfer processes were characterized. In ^{31}P NMR, **1** and **2** exhibit AB and AMX patterns, respectively, due to spin–spin couplings between the chemically inequivalent phosphorus nuclei (Chart 1).

One promising approach for quantum information processing (QIPs) using entangled states of two level quantum systems (qubits) is to utilize nuclear spins because they show relatively longer coherence.[4] Liquid-state NMR-QIPs enable implementation of quantum algorithms under ordinal conditions,[5] whereas several solid-state QIP devices with entangled nuclear spins under cryogenic conditions have been fabricated under cryogenic conditions.[6,7] The qubit molecule utilized for Shor's factorization composed of five ^{19}F and two ^{13}C nuclei[8] is ideal for the NMR-QIPs: each $I = 1/2$ inequivalent nucleus exhibits spin–spin couplings with the other nuclei, and the spin–spin coupling constants are larger than reciprocals of T_2 (spin–spin relaxation) values. However, with only second-row elements, it will become difficult to utilize larger numbers of qubits for NMR-QIPs. As the number of nuclei increases, differences of resonance frequencies and spin–spin couplings become smaller, and selective operation of qubits and creation of entanglements are expected to be hard.

In the course of our studies on **1** and **2** in terms of material development, we focused on QIPs by use of the ^{31}P nuclei ($I = 1/2$, 100% natural abundance). Phosphorus nuclei show a variety of chemical shifts[9] and large spin–spin couplings, which would be suitable to develop novel qubit molecules in the future. In this paper, we report some ^{31}P NMR experiments leading to QIPs by use of **1** and **2**, proving that ^{31}P nuclei are available for liquid-state NMR-QIPs.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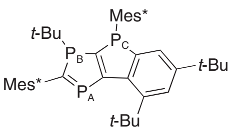
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Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$

Chart 1.

Table 1. ^{31}P NMR parameters of **1**[a]

Nucleus	δ	$^2J_{PP}$/Hz	T_1/s	T_2/s	T_2^{-1}
P$_A$	23.42	25.86	1.53	0.21	4.76
P$_B$	53.95	—	0.73	0.22	4.55

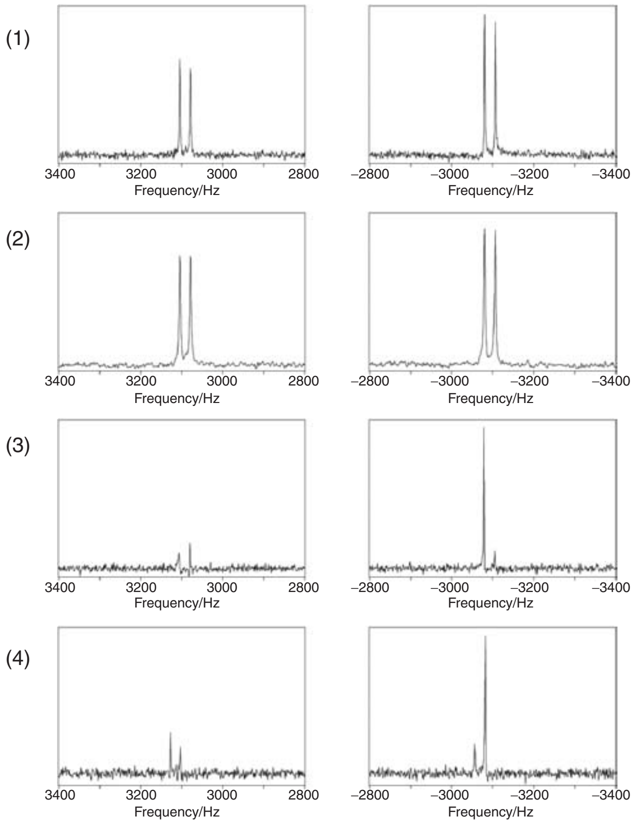
[a]In C$_6$D$_6$ at 25 °C.

Table 1 summarizes ^{31}P NMR properties of **1** of two inequivalent sp^3 phosphorus nuclei.[10] T_1 and T_2 data were determined by inversion recovery[11] and Carr–Purcell–Meiboom–Gill methods,[12] respectively. The reciprocals of T_2 are smaller than $^2J_{PP}$, indicating that decoherence can be avoided in NMR-QIP operations.

To evaluate usefulness of **1** for NMR-QIPs, we demonstrated implementation of the Deutsch–Jozsa (DJ) algorithm for distinguishing between "constant" and "balanced" $f(x)$ functions.[13] In the DJ algorithm with N bits system, the function is constant if $f(x)$ is independent of inputs (x) and it is balanced if $f(x)$ is zero for half of the inputs and unity for the other half. Whereas classical computers would calculate up to $2^{N-1} + 1$ times for checking whether $f(x)$ is constant or balanced, the quantum calculation distinguishes constant or balanced by single operation. In this study, we employed a ^{31}P version of the Freeman pulse sequences[14,15] for implementation of two-qubit DJ algorithm. Figure 1 summarizes ^{31}P NMR-QIP results for **1**. The f_1 and f_2 of constant functions, using a unity operation and P$_A$ (work) selective π pulse respectively, show almost the same spectra as normal measurements of **1**. On the other hand, f_3 and f_4 of balanced with selective π pulses on one of the peaks of the work qubit ($|\downarrow\uparrow\rangle \rightarrow |\downarrow\downarrow\rangle$ and $|\uparrow\uparrow\rangle \rightarrow |\uparrow\downarrow\rangle$), the peaks of input (P$_B$) qubit disappeard. Thus, we succeeded in distinguishing constant and balanced functions for 2-qubit DJ algorithm with two ^{31}P nuclei of **1**.

We next investigated ^{31}P NMR properties of **2** bearing both sp^2 and sp^3 phosphorus atoms.[3] Table 2 summarizes ^{31}P NMR parameters of **2**. As for T_1 and T_2 data, the sp^2 phosphorus exhibits considerably rapid decoherence in comparison with the remaining sp^3 phosphorus probably due to anisotropic effects of shielding coefficients.[16] However, the parameters in Table 2 indicate that **2** is available for NMR-QIPs.

We attempted creation of pseudopure states[15] by use of **2**, leading to implementation of several QIP algorithms. Although experimental results were not ideal (see Supporting Information),[17] the obtained spectrum indicated that NMR-QIPs with **2** are basically possible.



x	f_1	f_2	f_3	f_4
0	0	1	0	1
1	0	1	1	0

Figure 1. $^{31}P\{^1H\}$ NMR spectrum (C_6D_6) after implementation of the Deutsch–Jozsa algorithm on **1**. Frequency is in hertz with respect to Larmor frequency of an average between each nucleus. (1) and (2): constant functions (f_1, f_2); (3) and (4): balanced functions (f_3, f_4). Conditions: 202 MHz, offset 38.685 ppm, sweep 100 ppm, scan 1 time.

Table 2. ^{31}P NMR parameters of **2**[a]

Nucleus	δ	J_B/Hz	J_C/Hz	T_1/s	T_2/ms	T_2^{-1}
P_A	247.28	43.6	26.2[b]	0.080	50	20
P_B	83.51	—	49.5	1.100	130	7.69
P_C	−6.81	—	—	0.778	746	1.34

[a]In C_6D_6 at 25 °C. [b]Relative sign is opposite to the other constants.

In summary, we have demonstrated fundamental experiments for ^{31}P NMR-QIPs by using **1** and **2** as qubit molecules. Attempts to design and synthesize of novel qubit molecules and implementation of quantum algorithms are in due course.

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References and Notes

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10 Samples employed for NMR experiments were dissolved in C_6D_6, degassed via the freeze–vacuum procedures, and sealed. ^{31}P NMR data were recorded on a JEOL JNM-ECP-500A spectrometer with H_3PO_4 as external standard at 25 °C.

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17 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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