Entanglement Control of Azobenzene by Photoisomerization in NMR Quantum Computer

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Abstract

Entanglement control of qubits in a photoisomerizing molecule is studied in the context of an NMR quantum computer by taking azobenzene as an example. Azobenzene has two different isomers, trans-azobenzene (TAB) and cis-azobenzene (CAB), which can be interconverted by photoisomerization. Changing molecular structure leads to change in the spin-spin coupling constant, and hence leads to change in entangling operation time. We first obtain stable structures of TAB and CAB by \textit{ab initio} calculation. Then, we calculate the NMR spectra of these isomers and verify that they reproduce the chemical shift obtained experimentally with a good precision. Our result indicates that the coupling strength between a $^{15}$N and a $^{13}$C nuclei in the molecule changes by a large amount under photoisomerization.
INTRODUCTION

Quantum computer utilizes quantum mechanical phenomena, such as superposition and entanglement, as computational resources to outperform current digital computers. Nonetheless, a working quantum computer is yet to be realized. Feynman proposed the possibility of a quantum computer for the first time [1] and Deutsch triggered quantum computer research by introducing a quantum Turing machine [2]. Shor’s algorithm [3] and Grover’s algorithm [4] demonstrated that a quantum computer can process some practical problems more efficiently than a classical computer by making use of an exponentially massive parallel processing, known as the quantum parallelism.

There are several physical realizations of a quantum computer proposed to date [5, 6]; trapped ions [7], neutral atoms in optical lattices [8], an NMR quantum computer [9], and superconducting qubits [10], among others. Nuclear spins in a molecule work as qubits, that are controlled by nuclear magnetic resonance (NMR) spectrometer in an NMR quantum computer [11]. An NMR quantum computer may have several qubits if an appropriate molecules are employed. $^{13}$C-labelled chloroform [12] works as a two-qubit quantum computer, for example.

Controlling the coupling between nuclear qubits in a molecule by structural change has been already attempted [13]. In this paper, we analyze molecules whose inter-qubit coupling can be controllable by photoisomerization. Azo compounds are molecules whose two functional groups (aryl or alkyl) $\text{R}$ and $\text{R}'$ are connected by an azo group ($\text{N}=\text{N}$) as $\text{R}-\text{N}=\text{N}-\text{R}'$. They change their molecular structure between $\text{trans}$-azobenzene (TAB) and $\text{cis}$-azobenzene (CAB) under photoisomerization. Application of the photoisomerization of azobenzene to the switching device has been studied in [14, 17]. In fact, CAB is unstable and it gradually changes to TAB, although the relaxation time of this process is long enough to control qubits many times [18]. One of the advantages of using azobenzene for quantum computation is that it is possible to control interaction between qubits by changing molecular structure by UV light irradiation. It is the purpose of this paper to study the interaction between nuclei in azobenzene and to propose the possibility of using azobenzene or similar molecules as a multi-qubit NMR quantum computer with a tunable coupling.
THEORETICAL BACKGROUND

Let us consider a molecule with two spin-1/2 nuclei in a strong magnetic field $B_0$ along the $z$-axis. We assume that the nuclear species of the spins are different. The Hamiltonian of the molecule in the laboratory frame is

$$
\mathcal{H} = -\omega_{0,1} I_z \otimes I - \omega_{0,2} I \otimes I_z + \mathcal{H}_{\text{int}},
$$

where $I_k = \sigma_k/2$ is the $k$th component of the Pauli spin matrix divided by 2 and $\omega_{0,i}$ is the Zeeman energy of the $i$th spin. The interaction Hamiltonian between the spins is given by

$$
\mathcal{H}_{\text{int}} = \sum_{j,k=x,y,z} J_{jk} I_j \otimes I_k.
$$

Here $J_{jk}$ are called the spin-spin coupling constants (SSCC). The coupling constants $J_{jk}$ take the isotropic Heisenberg form $J_{jk} = J\delta_{jk}$ for a molecule in a liquid state at room temperature, which we assume to be the case throughout this paper. Then $\mathcal{H}_{\text{int}}$ simplifies as

$$
\mathcal{H}_{\text{int}} = J \sum_{k=x,y,z} I_k \otimes I_k.
$$

Let us fix the basis vectors as

$$
|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix},
$$

where $|0\rangle$ ($|1\rangle$) corresponds to the spin-up (spin-down) eigenstate of $\sigma_z$. We take the order of the two-qubit binary basis vectors as $\{|00\rangle, |01\rangle, |10\rangle, |11\rangle\}$ as usual. We transform the Hamiltonian in the laboratory frame to that in the rotating frame of each spin by introducing the unitary transformation

$$
U(t) = e^{-i\omega_{0,1} I_z t} \otimes e^{-i\omega_{0,2} I_z t}.
$$

The Hamiltonian in the rotating frame is

$$
\mathcal{H}_{\text{rot}} = U \mathcal{H} U^\dagger - iU \frac{d}{dt} U^\dagger
= J I_z \otimes I_z,
$$

where rapidly oscillating matrix elements have been dropped.
The time-evolution operator in this frame is

\[
U_{\text{rot}}(t) = e^{-iH_{\text{rot}}t} = \begin{pmatrix}
    e^{-iJt/4} & 0 & 0 & 0 \\
    0 & e^{iJt/4} & 0 & 0 \\
    0 & 0 & e^{iJt/4} & 0 \\
    0 & 0 & 0 & e^{-iJt/4}
\end{pmatrix},
\]

(7)

where we have taken the natural unit, in which \( \hbar = 1 \). Suppose the initial state is a product state \( |+0\rangle = \frac{1}{\sqrt{2}}(|00\rangle + |10\rangle) \), for example, where \( |\pm\rangle \) are the eigenvectors of \( \sigma_x \) with the eigenvalues \( \pm 1 \). This state may be generated by applying the Hadamard gate on the first qubit of a state \( |00\rangle \), for example. The action of \( U_{\text{rot}}(t) \) on \( |+0\rangle \) yields the state

\[
U_{\text{rot}}(t)|+0\rangle = \frac{1}{\sqrt{2}} \left( e^{-iJt/4}|00\rangle + e^{iJt/4}|10\rangle \right) = \cos \left( \frac{Jt}{4} \right) |+0\rangle - i \sin \left( \frac{Jt}{4} \right) |-0\rangle.
\]

(8)

This shows that the spins are in a maximally entangled state (MES) at \( t = \tau \) such that \( |\cos(J\tau/4)| = |\sin(J\tau/4)| \), that is,

\[
\tau = \frac{\pi}{|J|} (2n + 1), \quad (n = 0, 1, 2, \ldots).
\]

(9)

**METHOD**

Stable structures and vibrational properties of azobenzene were already reported in [19], in which Gaussian03 with density functional theory (DFT) and Møller-Plesset (MP) methods were employed. We used DFT method in the present work since MP method fails to calculate SSCC. First, we evaluated optimized structures of azobenzene with DFT calculation: B3LYP [20, 21], B3PW91 [21, 22], PW91PW91 [22] and PBEPBE [23] with basis set: 6-31+G(d).

Next, we calculated the NMR spectrum and SSCC of azobenzene using Gauge-Independent Atomic Orbital (GIAO) method [24–27] and Integral-Equation-Formalism Polarizable Continuum Model (IEFPCM) method [28, 29]. GIAO method was employed to calculate the NMR spectrum, while IEFPCM method was used to take account of the solvent effect of chloroform in our calculation. Chemical shifts of carbons are relative to tetramethylsilane (TMS) and those of nitrogens are relative to ammonia (NH₃).
RESULTS

We calculated stable structures of azobenzene with Gaussian03 with B3LYP/6-31+G(d), B3PW91/6-31+G(d), PW91PW91/6-31+G(d) and PBEPBE/6-31+G(d). The results obtained reproduce the previous ones with a good precision (data not shown). Figure shows the schematic structures of TAB and CAB. We studied entanglement between a nitrogen nucleus and a carbon nucleus, which are denoted as nuclei 1 and 7 in Fig. (a), and 1’ and 7’ in Fig. (b), respectively. It should be noted that the N=N-C angle changes drastically by photoisomerization, under which the molecule transforms between TAB and CAB. We note from the NMR spectra of two nitrogen nuclei that they are very weakly coupled, that is \( J \approx 0 \) for this pair, and hence it is takes extremely long time to entangle these nuclei.

Table I shows the chemical shifts of the nitrogen and the carbon nuclei and SSCC between them we have obtained. They are computed with DFT functionals with B3LYP/6-31+G(d), B3PW91/6-31+G(d), PW91PW91/6-31+G(d) and PBEPBE/6-31+G(d). The times to attain the maximal entanglement were calculated with Eq. (9) by setting \( n = 0 \).

Experimentally measured values of the chemical shifts of the carbon and the nitrogen nuclei are also given in Table I. The calculated chemical shifts of carbon nuclei reproduce the experimental results fairly accurately, while those of nitrogen nuclei do not agree with the experimental results with a good precision. This difference might be attributed to the difference in experimental conditions. The observed chemical shifts of carbon nuclei were obtained for azobenzene in liquid chloroform solvent, while those of nitrogen nuclei were obtained for azobenzene in a polycrystalline state.

Experimental values of SSCC between the nitrogen and the carbon nuclei in azobenzene do not exist to our knowledge. In contrast, the measured data of SSCC between carbon nuclei are available and they are in good agreement with our computational results (data not shown). We expect, from these evidences, that the computed SSCC between the nitrogen and the carbon nuclei are reliable. Time to produce MES in CAB is longer than that of TAB in all computational results. The ratio of times required to attain MES in CAB to that of TAB depends on the scheme; it is 4.2, 3.6, 2.3 and 2.4 with B3LYP, B3PW91, PW91PW91 and PBEPBE, respectively.

In this work, we have employed azobenzene to propose the possible application of pho-
toisomerizing molecules to an NMR quantum computer. The results showed that the time required to attain MES changes by a large amount between the two isomers, CAB and TAB. This suggests that photoisomerization can be used to control SSCC, and hence entanglement in azobenzene, which is potentially a powerful tool in NMR quantum computing.

CONCLUSION AND DISCUSSION

We calculated the time required to attain maximal entanglement between the carbon and nitrogen nuclei in azobenzene with \textit{ab initio} methods. As a result, the time to attain maximal entanglement in \textit{cis}-azobenzene is approximately four times longer than that in \textit{trans}-azobenzene. This reflects the fact that SSCC of \textit{cis}-azobenzene is four times weaker than that of \textit{trans}-azobenzene. We conclude that azobenzene can be employed as a molecule with a tunable coupling in NMR quantum computing.

Search for photoisomerizing molecules with a more drastic change in SSCC under photoisomerization is in progress and will be reported elsewhere.

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FIG. 1: Schematic structures of trans-azobenzene (a) and cis-azobenzene (b).
TABLE I: Chemical shift, spin-spin coupling constant and time to attain maximally entangled state of trans-azobenzene (upper table) and cis-azobenzene (lower table). aChemical shift of nitrogen nucleus (7 and 7') and bchemical shift of carbon nucleus (1 and 1'). Experimental values are from cRef. [31], dRef. [30], and eRef. [32]. The value of $J(12, 16)$ is an average of calculated $J(12)$ and $J(16)$ since the experimentally available value is an average of $J(12)$ and $J(16)$. This also applies to $J(1'2', 1'6')$.

|                | N(7)  | C(1)  | $J(12, 16)$ | $J(17)$ | $\tau$ |
|----------------|-------|-------|-------------|---------|--------|
| B3LYP          | 504   | 157   | 37          | -3.8    | 0.84   |
| B3PW91         | 501   | 153   | 35          | -4.5    | 0.70   |
| PW91PW91       | 486   | 157   | 33          | -8.9    | 0.35   |
| PBEPBE         | 486   | 156   | 33          | -8.5    | 0.37   |
| Experiment     | 509c  | 153d  | 34d         |         |        |

|                | N(7') | C(1') | $J(1'2', 1'6')$ | $J(1'7')$ | $\tau$ |
|----------------|-------|-------|-----------------|-----------|--------|
| B3LYP          | 547   | 159   | 37              | -16       | 0.20   |
| B3PW91         | 542   | 155   | 36              | -16       | 0.20   |
| PW91PW91       | 525   | 158   | 34              | -21       | 0.15   |
| PBEPBE         | 524   | 158   | 34              | -20       | 0.15   |
| Experiment     | 529e  | 154d  | 32d             |           |        |