Magnetism of aromaticity expected in Diels-Alder reaction

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Abstract – Diels-Alder reaction, which is driven by the ring current in the classical picture, could show the physics analogous to benzene characterized by the large diamagnetic susceptibility perpendicular to the molecular plane. However, the magnetic property of Diels-Alder reaction has not been studied well. In this study, expecting the possibility of the application for the magnetic field generation, we tried to observe the ring current in Diels-Alder reaction by the magnetization measurement. Contrary to the expectation, the increase of the magnetization was observed as the reaction proceeded. As a result of analysis, it is concluded that the increase of the magnetization is originated from the change of the number of C=C double bondings and not related to the ring current. Despite the observation of the ring current is failed, in-situ visualization of the reaction is realized by monitoring the change of magnetic susceptibility.

1. Author information

T. Nomura: Specialty is the solid state physics in ultrahigh magnetic fields. In this study, he is responsible for the concept of the study and the magnetization measurement.
H. Suzuki: Specialty is the synthetic organic chemistry. In this study, he is responsible for the choice of the reaction and its kinetics.

2. Concept and purpose

2.1 Ultrahigh magnetic field generation

Flux compression is known as the most successful method which enables to generate ultrahigh magnetic field over 100 T by the sacrifice of the coil destruction[1], [2]. Figure 1 shows the schematic of this method. In advance, the initial seed magnetic field ($B_0 \sim 3$ T) is generated inside the liner which is made by copper. When the external force drives the liner shrinkage, magnetic fluxes filled in the liner are confined in small area. Because the magnetic field corresponds to the density of the magnetic flux, the final magnetic field (B_1) is proportional to the ratio of the area (S_0/S_1).

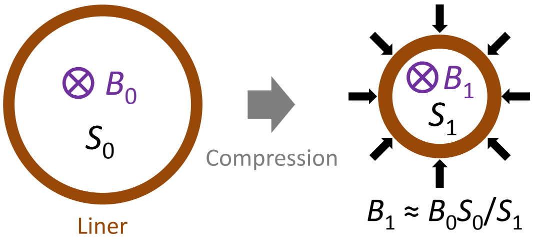

Fig. 1 Schematic of the flux compression.

For the generation of the extremely high magnetic field using the flux compression, it is essential to confine the flux in the area as small as possible. This is also suggested by the fact that the energy of the static magnetic field is obtained by the volume integral of $B^2/(2\mu_0)$. In other words, the high field generation in small area is rather easy than that in large area. This is an important concept to realize extreme conditions not only in high field but also in high pressure using a diamond anvil cell. Therefore, if the area of the field generation could be extremely small area as the scale of one atom or one molecule, it might be possible to realize an unprecedented field strength. From such a viewpoint, we get the idea to utilize the ring current in a benzene circle for the ultrahigh magnetic field generation.

2.2 Benzene and ring current

Benzene is the most simple aromatic hydrocarbon, where the double bondings are resonating as Fig. 2. Thus, the π electrons of carbon are delocalized and generate ring current when the magnetic field is applied. The ring current, which cancels the applied magnetic field, leads to a strong diamagnetism perpendicular to the molecular plane.

If we could manipulate the ring current freely, a new type of field generation technique might be possible. For example, by the radiation of the circularly-

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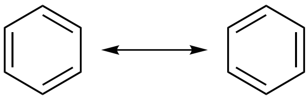

Fig. 2 Resonating picture of benzene.

polarized light whose energy corresponds to the energy level of the molecule, angular momentum could be controlled. Because the resonating π bonding state is similar to the physics of superconductor, magnetic flux induced by the ring current might be quantized (a). If one quantum flux is confined in a benzene circle, the locally generated magnetic field could be reached up to 10^4 T order. In next section, we consider the approach using chemical reaction.

2. 3 Diels-Alder reaction

The ring current characterizing benzene could also be generated by chemical reaction as Diels-Alder reaction (Fig. 3). This reaction is proceeded by the cooperative hopping of π electrons in a circular form and produces cyclic compound. This picture has a common feature with the ring current in the benzene circle, and the Diels-Alder reaction could be regarded as a reaction driven by the ring current. If the ring current is generated as Fig. 3, this system could be applied for the local magnetic field generation.

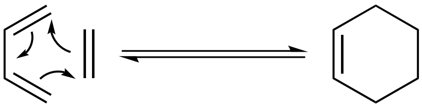

Fig. 3 Diels-Alder reaction.

However, it has not been examined whether the ring current really occurs or not in the Diels-Alder reaction. Because the Diels-Alder reaction is cooperative, the lifetime of the intermediate state is short and it is impossible to detect by slow measurement as NMR. Thus, the existence of the ring current as Fig. 3 is just a hypothesis to explain the experimental result and not validated. At least, it is unusual that only one direction of the ring current is induced, and the opposite direction should also occur in the same way. We guess that the resonating hopping of electrons as seen in benzene is realized.

2. 4 Purpose

As we stated above, it might be possible to utilize the Diels-Alder reaction, where the ring current is expected to occur, for a prospective magnetic field generation technique. However, there has not been an evidence that the ring current is really induced in the process of the Diels-Alder reaction. In this study, for the further understanding of the Diels-Alder reaction, we tried to confirm the existence of the ring current.

If the ring current exists, it could be detected by the macroscopic magnetization measurement as enhanced diamagnetism. Such enhanced diamagnetism is expected to contribute to the time- and space-averaged macroscopic magnetization. If an additional diamagnetic contribution to the reagent is detected, it could be attributed to the effect of the ring current. The additional diamagnetism is expected to be proportional to the rate of the Diels-Alder reaction. In other words, the reaction could be monitored in real time by the magnetization measurement.

Recently concerning the magnetization measurement, automatic measurement system employing SQUID (Superconducting QUantum Interference Device) is popularly used and make it possible to resolve the tiny magnetization as small as 10^{-8}emu order. Because the magnetic anisotropy of benzene reaches up to $\Delta\chi \equiv \chi_{\perp} - \chi_{\parallel} = -49 \times 10^{-6}$emu/mol[6], it is not hopeless to detect the additional diamagnetic contribution from the ring current in the Diels-Alder reaction. In addition, for the prospective study on the microscopic ultrahigh magnetic field, SQUID is considered to be an appropriate tool.

This report is constructed as below. In Chapter 3, we choose the reagents of the Diels-Alder reaction and obtain the basic information about its kinetics. In Chapter 4, magnetization of each reagents is measured and the accuracy of the measurement system is evaluated. In Chapter 5, magnetization measurement is conducted for the Diels-Alder reaction and we discuss whether the additional diamagnetic contribution from the ring current is observed or not. Finally in Chapter 6, the summary of this study is stated.

(a): For the case of benzene, quantization condition is not realized because of the topology of molecular orbital[5].

3. Choice of chemical reaction and its kinetics

3.1 Choice of reaction condition

First of all, we chose reagents of Diels-Alder reaction for this study. In choice of them, we focused on isoprene and acrolein that are commercially available and cheap (Fig. 4). In addition, they have been used for a long time as reagents of Diels-Alder reaction. Thus, we considered using them were appropriate for the purpose of this study.

Fig. 4 Diels-Alder reaction using isoprene and acrolein.

In initial screening, we conducted the Diels-Alder reaction using acrolein and isoprene without any solvent. Unfortunately, the reaction did not proceed at all even when the temperature was changed from 0°C to 35°C. Then, screening of additive was conducted for the reaction to proceed smoothly. In 1994, Cativiela reported that the reaction proceeded well by adding 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as solvent[7]. However, addition of solvent leads to increase of background noise when the reaction is analyzed by MPMS. Thus, we tried to optimize the condition by decreasing the amount of HFIP as less as possible. The optimized procedure is mixing isoprene (300 μL, 3 equivalent) and acrolein (67 μL, 1 equivalent) in HFIP (210 μL, 2 equivalent) at room temperature. We found that when the reaction was conducted in the procedure, approximately 50% yield of the product was obtained in 2 h. By contrast, we also found that the reaction did not proceed to afford only 4% yield at 0°C in 2 h.

3.2 Kinetics

Next, we tried to determine half-life of acrolein in the optimal condition (mixing isoprene (300 μL, 3 equivalent) and acrolein (67 μL, 1 equivalent) in HFIP (210 μL, 2 equivalent) at room temperature) for the quantitative evaluation of data in MPMS. For the evaluation, we checked the yield of the product in several times (1, 2, 4, and 6 h). In this study, the yield was determined by using ^{1}H NMR where durene was used as internal standard. Reaction rate equation of this system is shown as below;

$$v = k[\mathrm{iso}][\mathrm{acr}], \tag{1}$$

k; rate constant, [iso]; concentration of isoprene, [acr]; concentration of acrolein. Thus, the integrated form is shown as below;

$$\ln([\mathrm{acr}]_0[\mathrm{iso}]/[\mathrm{iso}]_0[\mathrm{acr}]) = ([\mathrm{iso}]_0 - [\mathrm{acr}]_0)kt, \tag{2}$$

$[\mathrm{iso}]_0$; initial concentration of isoprene, $[\mathrm{acr}]_0$; initial concentration of acrolein, t; elapsed time. The yield of the product is obtained from $[\mathrm{acr}]_0 - [\mathrm{acr}]$. The half-life of acrolein was determined as $\tau = 1.97 \pm 0.58$ h by fitting the experimental results using the equation (Fig. 5). Therefore, it can be said that roughly 50% yield of the product is obtained in 2 h.

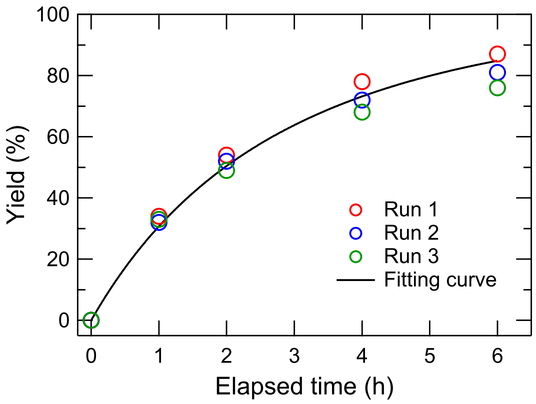

Fig. 5 Time dependence of the yield estimated from NMR and its fitting curve.

4. Magnetic susceptibility of reagents

Prior to the experiment on the Diels-Alder reaction, magnetic susceptibility of each reagents were measured to establish the experimental setup and estimate its accuracy. In this chapter, the experimental setup is shown and the accuracy of the measurement is discussed.

4.1 Magnetization measurement and analytical procedure

For the magnetization measurement, MPMS-XL7L (Magnetic Property Measurement System, Quantum Design Inc.) was used. To increase the signal from diamagnetic sample, the measurements were conducted at the maximum field of the system 7 T. The time dependence of the magnetization was monitored by repetitive measurements at isothermal condition.

The sample was encapsulated in the silica tube (inner diameter=6 mm, thickness=1 mm, length=10 cm) and sealed by O ring as Fig. 6. Generally, metallic parts have large magnetic susceptibility and need to be keep away from sample area (more than 5 cm). The encapsulated sample was attached to the bottom of a metal pipe and measured in the conventional way[8]. The time taken from the sample preparation to the measurement was approximately 2 min.

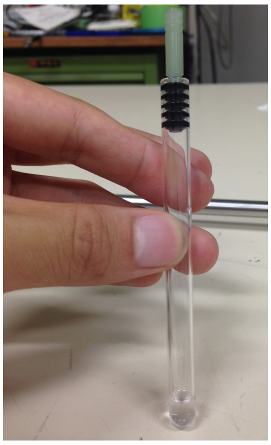

Fig. 6 Reagents encapsulated in the silica tube.

In this measurement, because the diamagnetic signal from the reagents is small and the silica tube causes an asymmetric background, it is necessary to subtract the background signal from raw data[9]. One example of the measurement on isoprene at the condition of 132.3 mg and −23°C is shown in Fig. 7. From the raw data on the silica tube and reagents (A), the background (B) is subtracted, and the sample signal (C) is obtained. By fitting the curve (C) as the reference[9], the value of the magnetization is calculated.

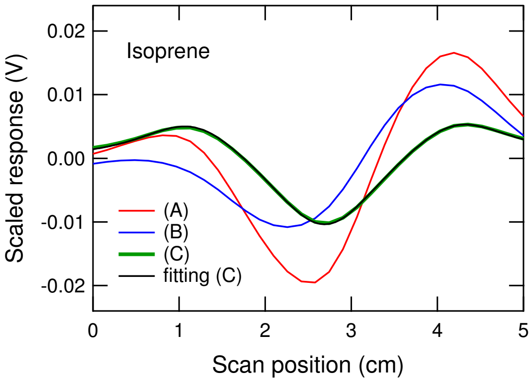

Fig. 7 Raw data in MPMS. (A) silica tube and reagents, (B) silica tube, (C) reagents and its fitting curve.

4.2 Magnetic susceptibility of reagents and evaluation

Here we show the results of isoprene and aclorein obtained by the setup stated above. To estimate the experimental accuracy, the same measurement was conducted also for methyl acrylate. We suppose that the diamagnetic susceptibility does not depend on the temperature, and deal with the data at different temperatures in a same way. The obtained susceptibility is compared to the estimated value using Pascal's constant (b)[11], [12].

The obtained results are shown in Table 1 with the estimated values by Pascal's constant. The temperature and the number of measurements (N) are also shown. Error bars are estimated assuming Student's t distribution at the reliability of 90%. The main source of the error is the evaporation of the reagents which causes the decrease of the weight. In addition, some amount of the reagent sticks on the wall of the silica tube and does not contribute the signal. The error sources stated above are inevitable in this measurement and it is necessary to be taken into account in the analysis. We estimate that the error of the absolute value of the magnetization is within 3%. For the case of relative value of the magnetization, we estimate that the error is less than 1% even in 3 h measurement.

The experimental results show good agreement with the estimated values from Pascal's constant except for isoprene where the experimental result is 10% larger than the estimated value. However the data shown in the database[10] is 46.0 (10^{-6}emu/mol) and within the error of the obtained result. The tendency of the overestimation could be due to the effect of evaporation. In three reagents, isoprene has the lowest boiling temperature and is easy to evaporate. Therefore, the resultant molar susceptibility tends to be estimated larger.

From the measurements stated above, it is shown that the small diamagnetic moment of the reagents can be measured by MPMS. The estimated accuracy is 3% for the absolute value and less than 1% for the relative value in 3 h measurement.

(b): The diamagnetic susceptibility is roughly obtained by the summation of the orbital contributions of each elements. Pascal's constant is a semi-empirical diamagnetic value of the element, and the resultant diamagnetic susceptibility can be estimated by the elemental composition. However, if a conjugated state exist, some corrections are required.

Table 1 Magnetic susceptibility of the reagents obtained by the experiment and Pascal's constant [11], [12].

Reagent	Experiment (10^{-6}emu/mol)	Pascal (10^{-6}emu/mol)	N	T (°C)
Isoprene	-48.7 ± 1.4	-42.84	3	-23, 0
Acrolein	-27.5 ± 0.8	-28.27	5	0, 22
Methyl acrylate	-45.6 ± 1.2	-45.34	4	0

5. Time dependence of the magnetization in Diels-Alder reaction

In this chapter, we report the magnetism of the Diels-Alder reaction using the reagents chosen in Chapter 3. Firstly, the typical time evolution of the magnetization of the reaction is shown in Fig. 8. The experimental condition is denoted in the graph. As the reaction proceeds, the diamagnetic moment increases exponentially and finally saturates. This tendency has not been observed in the measurements of each reagents. By the exponential curve fitting, the half-life of the time evolution is obtained as $\tau = 3.6 \pm 1.5$ h ($N = 3$) and corresponds to that obtained in NMR. Furthermore, it is confirmed that the change of the magnetic moment does not occur at 0°C where the reaction stops. Therefore, it is concluded that the change of the magnetization shown in Fig. 8 is caused by the progression of the reaction.

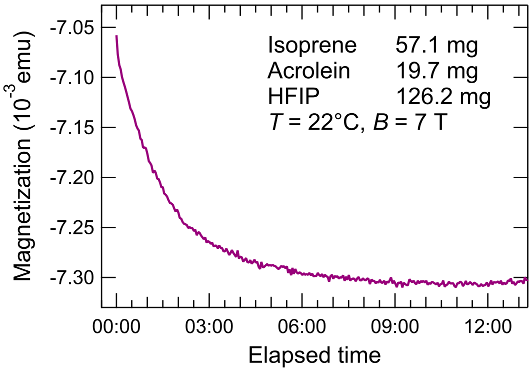

Fig. 8 Typical time evolution of the magnetization of the Diels-Alder reaction.

Here, we discuss the reason why the diamagnetic moment increases. If it is caused by the ring current, diamagnetic susceptibility should decrease as the reaction proceeds. Evaporation of the reagents from the silica tube should also cause the decrease of the diamagnetic moment. Therefore, the increase of the diamagnetic moment is attributed to the other reasons than our expectation.

As a result of analysis, it is suggested that the observed change of the diamagnetic moment is caused by the change of chemical bonding. When Diels-Alder reaction occurs, two C=C double bonds change to C−C single bonds. In Pascal's constant, there is "constitutive correction factor" reflecting the different chemical bonding in addition to the elemental composition. When two C=C change to C−C, $\Delta\chi = -11.0 \times 10^{-6}$emu/mol is expected[11], [12]. At the condition of Fig. 8, $\Delta M = -0.27 \times 10^{-3}$emu is expected in the case for 100% yield, corresponding to the experimental value $\Delta M = -0.25 \times 10^{-3}$emu. Therefore, the increase of the diamagnetic moment in Fig. 8 is explained by the different magnetic susceptibility of the reagents and product. Such a magnetization change in a chemical reaction is reported in 1930's using Gouy method and proposed to be applicable to monitor the rate of chemical reaction[13], [14]. From the viewpoint of resolution, SQUID is better than Gouy method and it can be said that the method in this study is more useful to monitor the chemical reaction.

Here, it is hopeless to subtract the effect of chemical bonding change and obtain the tiny signal from the ring current. As shown in Chapter 4, the error of the absolute value of the magnetization is as much as 3% and accurate subtraction of the background signal is impossible. Additionally, the rate of the reaction has a large error as shown in the result of NMR. Even if the accuracy improves, it seems difficult to subtract the effect of chemical bonding change.

6. Summary

In this study, the time evolution of the magnetization in the Diels-Alder reaction is measured to observe the ring current. Because of the experimental error and the increase of the diamagnetic moment caused by the chemical bonding change, the ring current could not be detected. However, by monitoring the increase of the diamagnetic moment, in-situ monitoring of the progression of the chemical reaction is achieved. This is the first example to utilize SQUID for such a monitoring as far as our knowledge.

In this study, we used the macroscopic magnetization measurement expecting the possibility of the application for the local magnetic field generation. However, it might be appropriate to use a microscopic probe as optical measurement if the observation of the ring current itself is a purpose. In that case, it is necessary to use high frequency light as to follow the time scale of the reaction.

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Reference

[1] F. Herlach and N. Miura eds., *"High magnetic fields, science and technology"* Vol. 1-3, (World Scientific, 2003-2006).

[2] S. Takeyama, E. Kojima, J. Phys. D: Appl. Phys. **44**, 425003 (2011).

[3] Y. H. Matsuda, Y. Ueda, H. Nojiri, T. Takahashi, T. Inami, K. Ohwada, Y. Murakami, T. Arima, Physica B Condens. Matt. **346**, 519 (2004).

[4] K. Mackay, M. Bonfim, D. Givord, A. Fontaine, J. Appl. Phys. **87**, 1996 (2000).

[5] N. Byers, C. N. Yang, Phys. Rev. Lett. **7**, 46 (1961).

[6] L. Pauling, J. Chem. Phys. **4**, 673 (1936).

[7] C. Cativiela, J. I. Garcia, J. A. Mayoral, L. Salvatella, Can. J. Chem. **72**, 308 (1994).

[8] Magnetic property measurement system user's manual `http://www.mrl.ucsb.edu/sites/default/files/mrl_docs/instruments/fundmanual.pdf`.

[9] MPMS application note 1014-213 `http://www.qdusa.com/sitedocs/appNotes/mpms/1014-213.pdf`.

[10] D. R. Lide, *"CRC handbook of chemistry and physics"* 87th edition, (CRC Press, 2006) 3-673.

[11] R. L. Charlin, *"Magnetochemistry"*, (Springer-Verlag, 1986) 3.

[12] O. Kahn, *"Molecular magnetism"*, (VCH, 1993) 3.

[13] P. W. Selwood, *"Magnetochemistry"* 2nd edition, (Interscience Publishers LTD, London, 1956).

[14] J. Farquharson, Trans. Faraday Soc. **32**, 219 (1936).