

## Observation of the Predicted *Negative Faraday A* MCD Term in a Cyclobutadiene Dianion

Kazuyuki Ishii, Nagao Kobayashi,\* Tsukasa Matsuo,†  
Masanobu Tanaka,† and Akira Sekiguchi†

Department of Chemistry, Graduate School of Science  
Tohoku University, Sendai 980-8578, Japan  
Department of Chemistry, University of Tsukuba  
Ibaraki 305-8571, Japan

Received December 19, 2000

The cyclobutadiene dianion (CBD<sup>2-</sup>) has been studied from both synthetic and theoretical viewpoints. According to Hückel's rule, the six  $\pi$  electrons of the CBD<sup>2-</sup> species are expected to show both aromaticity and planarity of the molecule. However, it has been pointed out that CBD<sup>2-</sup> derivatives may prefer distorted structures because of electronic repulsion originating from the large negative charge density per atom.<sup>1–6</sup> Hence, it has been a challenge to substantiate the existence of aromaticity in CBD<sup>2-</sup>.

Recently, we succeeded in synthesizing a dilithium salt of tetrakis(trimethylsilyl)cyclobutadiene dianion (**1**) (Chart 1) by taking advantage of the electronic and steric effects of the silyl groups, which can stabilize the dilithium salts of unsaturated organic compounds such as benzene and ethylene.<sup>8,9</sup> X-ray crystallographic analysis showed that the four-membered ring is planar and approximates to  $D_{4h}$  symmetry in the crystal, while <sup>6</sup>Li NMR spectroscopy revealed the existence of a strong aromatic ring current shielding effect. This was the first experimental evidence to confirm aromaticity of the CBD<sup>2-</sup> species. In addition, a simple calculation predicts that the aromatic CBD<sup>2-</sup> has six  $\pi$  electrons and four  $\pi$  orbitals ( $a_{2u}$ ,  $e_g$ , and  $b_{2u}$  orbitals as shown in Figure 1), resulting in degenerate highest occupied  $\pi$  molecular orbitals (HO $\pi$ MOs) and a nondegenerate lowest unoccupied  $\pi$  molecular orbital (LU $\pi$ MO). Since general aromatic organic compounds have either degenerate HO $\pi$ MOs and LU $\pi$ MOs, nondegenerate HO $\pi$ MO and degenerate LU $\pi$ MOs, or nondegenerate HO $\pi$ MO and LU $\pi$ MO, the CBD<sup>2-</sup> appears to have an unusual electronic structure, which warrants further investigation. The simultaneous use of UV–visible absorption and magnetic circular dichroism (MCD) spectroscopies is an excellent technique for elucidating this type of unusual electronic structure, as described below.<sup>10</sup> (1) When the four-membered ring has  $D_{4h}$

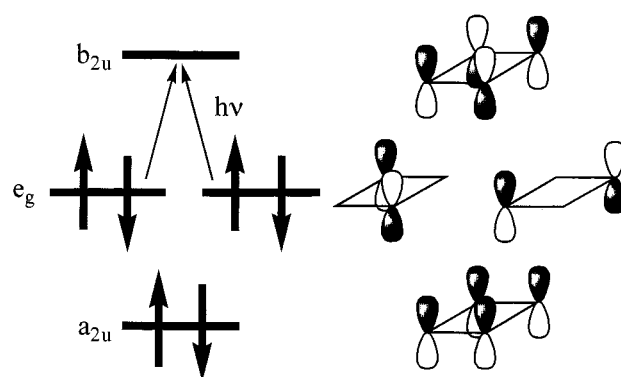
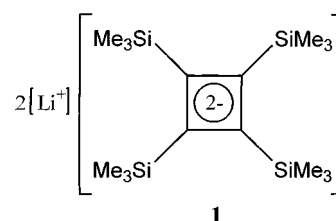


Figure 1.  $\pi$  molecular orbitals of the aromatic cyclobutadiene dianion.

### Chart 1



symmetry, the ground state is  $^1A_{1g}$ , and  $e_g \rightarrow b_{2u}$  excitations lead to  $^1E_u$  excited states. Since the degenerate  $^1A_{1g} \rightarrow ^1E_u$  transitions are electric dipole allowed, only one intense absorption is expected. Furthermore, the transitions to the degenerate states are easily discernible from the Faraday A term in the MCD spectrum, which confirms the high symmetry of the molecule. (2) The sign of the Faraday A term depends on the difference in the orbital angular momentum ( $L$ ) between the excited electron and electron hole. Since the MO energy is lowered with decreasing  $|L|$ , it is normally difficult to observe a negative A term due to the larger  $|L|$  of an electron hole in aromatic organic compounds. More than 20 years ago, Michl proposed that the  $^1A_{1g} \rightarrow ^1E_u$  transitions of an aromatic CBD<sup>2-</sup> species would be a good example of a characteristic negative Faraday A term, due to excitation from the degenerate  $e_g$  orbitals to the nondegenerate  $b_{2u}$  orbital.<sup>10</sup> However, because of the unavailability of stable CBD<sup>2-</sup>, no one has yet succeeded in presenting experimental evidence for this. In this paper, we report an investigation of the electronic absorption and MCD properties of compound **1**, which shows, for the first time, a clear negative Faraday A term for an aromatic organic compound.

Compound **1** was synthesized in dry oxygen-free tetrahydrofuran (THF) using a previously reported method.<sup>7</sup> After removal of THF in vacuo, the sample solution for measurements was prepared by vacuum transfer of degassed *n*-hexane. Electronic absorption spectra were measured with a Shimadzu UV-2100 spectrometer. **1** showed a peak at 289 nm with an absorption coefficient ( $\epsilon$ ) of  $6130 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . MCD measurements were made with a JASCO J-720 spectrodichrometer equipped with a JASCO electromagnet that produced magnetic fields of up to 1.1 T ( $T = \text{tesla}$ ) with parallel and then antiparallel fields.

UV–visible absorption and MCD spectra of compound **1** are shown in Figure 2. An intense absorption band is seen at 289 nm in the UV–vis spectrum.<sup>11</sup> In the MCD spectrum, two intense peaks of opposite sign are observed at 274.5 and 298 nm, and the inflection point coincides with the absorption maximum within experimental error. These are characteristic of a Faraday A term,

(11) A weak, broad absorption band which is assigned to the  $\pi \rightarrow \sigma^*$  transitions by the ZINDO/S calculations is seen at around 500 nm.

\* Address correspondence to this author at Tohoku University.  
† University of Tsukuba.

(1) McKennis, J. S.; Brener, L.; Schweiger, J. R.; Pettit, R. *J. Chem. Soc., Chem. Commun.* **1972**, 365.

(2) Garrat, P. J.; Zahler, R. *J. Am. Chem. Soc.* **1978**, *100*, 7753.

(3) (a) Boche, G.; Etzrodt, H.; Marsch, M.; Thiel, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 132. (b) Boche, G.; Etzrodt, H.; Marsch, M.; Thiel, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 133. (c) Boche, G.; Etzrodt, H.; Massa, W.; Baum, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 863.

(4) (a) Clark, T.; Wilhelm, D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1982**, *23*, 3547. (b) Hess, B. A., Jr.; Ewing, C. S.; Schaad, L. J. *J. Org. Chem.* **1985**, *50*, 5869.

(5) Skancke, A.; Agranat, I. *Nouv. J. Chim.* **1985**, *9*, 577.

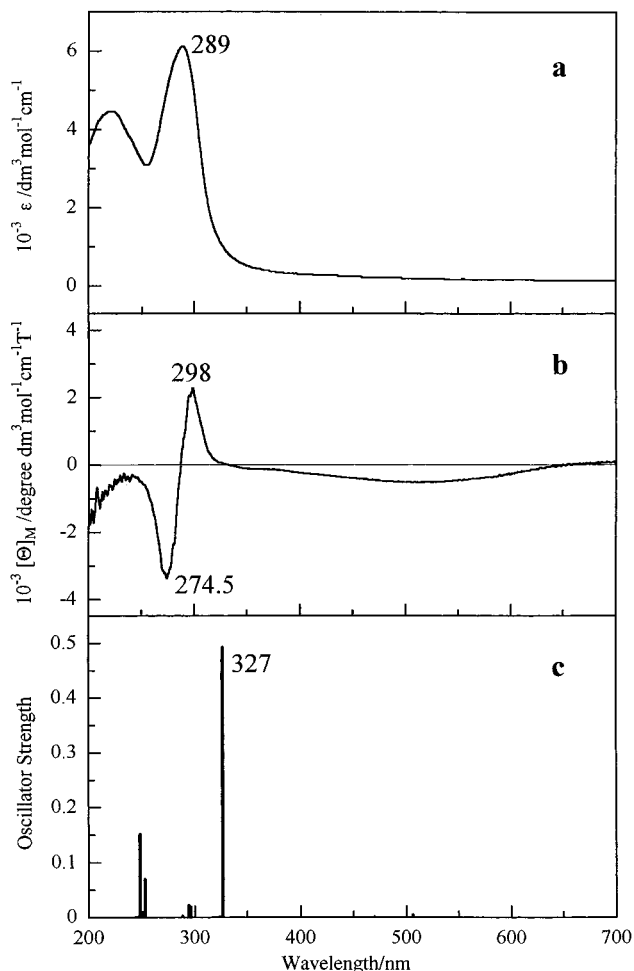
(6) (a) Zandwijk, G. v.; Janssen, R. A. J.; Buck, H. M. *J. Am. Chem. Soc.* **1990**, *112*, 4155. (b) Balci, M.; McKee, M. L.; Schleyer, P. v. R. *J. Phys. Chem. A* **2000**, *104*, 1246.

(7) Sekiguchi, A.; Matsuo, T.; Watanabe, H. *J. Am. Chem. Soc.* **2000**, *122*, 5652.

(8) (a) Sekiguchi, A.; Nakanishi, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 3748. (b) Sekiguchi, A.; Ichinohe, M.; Kabuto, C.; Sakurai, H. *Organometallics* **1995**, *14*, 1092. (c) Sekiguchi, A.; Ichinohe, M.; Takahashi, M.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1533.

(9) (a) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 1464. (b) Sekiguchi, A.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7081. (c) Ebata, K.; Setaka, W.; Inoue, T.; Kabuto, C.; Kira, M.; Sakurai, H. *J. Am. Chem. Soc.* **1998**, *120*, 1335.

(10) (a) Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6801. (b) Michl, J. *Tetrahedron* **1984**, *40*, 3845.



**Figure 2.** Electronic absorption (a) and MCD (b) spectra of compound **1** with the calculated spectrum (c). The spectrum was calculated using the ZINDO/S Hamiltonian.

indicating degenerate excited states. These spectroscopic characteristics suggest that compound **1** retains a high symmetry in *n*-hexane solution, and since the two MCD peaks at 298 and 274.5 nm exhibit positive and negative signs, respectively, the sign of the Faraday *A* term is clearly negative. The results are qualitatively interpreted as follows. When the  $\text{CBD}^{2-}$  exhibits aromaticity, three transitions, originating from the  $e_g \rightarrow b_{2u}$  and  $a_{2u} \rightarrow b_{2u}$  configurations, are possible. Since the transitions at 289 nm show an intense absorption band and a Faraday *A* term, they can be reasonably assigned to degenerate  ${}^1A_{1g} \rightarrow {}^1E_u$  transitions. The negative sign of the Faraday *A* term then originates from the  $e_g \rightarrow b_{2u}$  configuration, where the  $|L|$  of the electron hole (degenerate  $e_g$ ) is clearly larger than that of the excited electron (nondegenerate  $b_{2u}$ ).<sup>12</sup> MO calculations were carried out to enable a more quantitative discussion.<sup>13</sup> The optimum structure calculated

by the PM3 method has a planar and highly symmetric four-membered ring, indicating the existence of aromaticity. This aromaticity is explained by the small negative charge density on the four-membered ring ( $-1.16$ ) due to delocalization over the trimethylsilyl groups, which reduces the amount of electron repulsion. Configuration interactions were calculated for the optimum structure using the ZINDO/S Hamiltonian,<sup>14</sup> giving the spectrum shown in Figure 2. Although the calculation underestimates the transition energies, the intense absorption band at 327 nm, which consists mostly of the  $e_g \rightarrow b_{2u}$  configuration (91%), reproduces the experimental spectra nicely.<sup>15</sup>

In summary, we have studied the electronic properties of compound **1** using electronic absorption and MCD spectroscopies. The observed intense absorption band at 289 nm and the corresponding negative Faraday *A* term are interpreted by excitation from the degenerate  $e_g$  orbitals to the nondegenerate  $b_{2u}$  orbital, providing experimental evidence for the theoretical prediction of Michl.<sup>10</sup> To our knowledge, this is the first clear demonstration of the negative Faraday *A* term theoretically predicted for aromatic organic compounds.<sup>16–18</sup> This study is important not only as a rare example of a negative Faraday *A* term but also to illustrate the effectiveness of MCD spectroscopy in elucidating the chemistry of the  $\text{CBD}^{2-}$  species.

**Acknowledgment.** This work was supported by a Grant-in-Aid for Scientific Research (B) No. 11440192 and for Encouragement of Young Scientists No. 12740355 from the Ministry of Education, Science, Sports, and Culture, Japan.

JA004285R

(12) (a) Nyokong, T.; Gasyna, Z.; Stillman, M. J. *Inorg. Chem.* **1987**, *26*, 1087. (b) Piepho, S. B.; Schatz, P. N. *Group Theory in Spectroscopy, with Applications to Magnetic Circular Dichroism*; Wiley: New York, 1983. (c) To evaluate the magnetic moment ( $\mu$ ), band deconvolution analyses of the electronic absorption and MCD spectra were carried out using the program SIMPFIT.<sup>12a</sup> The  $D_0$ ,  $A_1$ , and  $\mu$  values of the negative Faraday *A* term were evaluated as 1.75,  $-1.30$ , and  $0.69$  using  $\langle \epsilon \rangle_0/326.6$ ,  $\langle \Delta \epsilon_M \rangle/152.5$ , and  $-0.9338(A_1/D_0)$ .<sup>12ab</sup> The  $\mu$  value is very close to that ( $=0.61$ ) calculated by Michl.<sup>10a</sup>

(13) MO calculations were carried out for compound **1** without lithium ions using *HyperChem R. 5.1* program (HyperCube Inc.).

(14) For the ZINDO/S calculations, the parameter 4 of silicon approximates to 11.11.

(15) One referee pointed out the necessity to include the lithium cations. Therefore, we have calculated configurational interactions of compound **1** including the lithium counterions using the AM1 Hamiltonian. As a result, the oscillator strength ( $f$  at 288 nm = 0.001) of the  $e_g \rightarrow a_{2u}$  (the  $a_{2u}$  orbital originates from the  $\text{Li}_{2s}-\text{Li}_{2s}$  antibonding-like orbital) transitions is less than 1% of that ( $f$  at 311 nm = 0.46) of the  $e_g \rightarrow b_{2u}$  transition. Therefore, the negative Faraday *A* term is clearly assigned to the  $e_g \rightarrow b_{2u}$  transition.

(16) (a) Stephens, P. J. *Symp. Faraday Soc.* **1969**, *3*, 40. (b) Waluk, J. W.; Michl, J. *Inorg. Chem.* **1981**, *20*, 963. (c) A negative Faraday *A* term has been observed for inorganic compounds ( $\text{Se}_4^{2+}$ ,  $\text{Te}_4^{2+}$ , and  $\text{S}_3\text{N}_3^-$ ). Here, the electronic properties of  $\text{Se}_4^{2+}$  and  $\text{Te}_4^{2+}$  are similar to that of the  $\text{CBD}^{2-}$ .<sup>16a</sup> and  $\text{S}_3\text{N}_3^-$  is a good example of symmetrically perturbed two- $\pi$  hole annulenes.<sup>10b,16b</sup>

(17) Complex MCD curves, which look like a negative *A* term, have been observed for benzene and tropylium ion.<sup>18</sup> Michl explained that these MCD spectra might result from magnetic moment borrowing.<sup>10</sup>

(18) (a) Allen, S. D.; Mason, M. G.; Schnepf, O.; Stephens, P. J. *Chem. Phys. Lett.* **1975**, *30*, 140. (b) Tajiri, A.; Hatano, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 962.