Synthesis, crystal structure and magnetic properties of *o*-carboranyl nitronyl nitroxide biradical: a prototype of a three-dimensional analogue of *o*-benzoquinodimethane

Fumiyasu Iwahori,^{a,b} Yoshikazu Nishikawa,^c Ken-ichiro Mori,^c Masahiro Yamashita^{b,d} and Jiro Abe*^a

Received 15th August 2005, Accepted 20th October 2005 First published as an Advance Article on the web 14th November 2005 DOI: 10.1039/b511579e

We have designed and synthesised a new carborane derivative containing two nitronyl nitroxides. This molecule can be considered as a prototype of a three-dimensional analogue of *o*-benzoquinodimethane. The magnetic susceptibility of a crystalline sample revealed that this biradical possesses a weak antiferromagnetic interaction ($\theta = -1.05(4)$ K) and an ESR study in frozen matrix in the 5.4–104 K range gave an intramolecular antiferromagnetic interaction of -27(2) K. The synthesis, physical properties and DFT calculation result are also reported.

Introduction

Considerable scientific efforts have been made on the chemistry of carboranes.1 Especially, owing to the characteristic icosahedral structure having remarkable stability, 1,2-dicarba-closo-dodecaborane derivatives have often been used as modules for supramolecular chemistry, organometallic chemistry, biochemistry and so on.² The substitution of the C-H hydrogen on the carborane cage has been achieved with the aim of the development of functionality. For example, a porphyrin-labelled carborane derivative has been synthesised as a pharmaceutical agent,^{3a} and a poly-(hydroxyl) substituted carborane was prepared for the improvement of the solubility in water.^{3b} Recently, we proposed a paramagnetic carborane derivative, the nitronyl nitroxide substituted carborane **OCB-NN** (= 1''-(4'-phenylene(3,3,4,4-tetramethvlimidazolyl-2-oxyl-5-oxide))-1",2"-dicarba-closo-dodecaborane, Chart 1(a); ortho-, $R_1 = NN$, $R_2 = H$).⁴ The head-to-tail dimer form of OCB-NN via hydrogen bonding was found in the crystal structure and an intradimer ferromagnetic interaction $(J/k_{\rm B} =$ +4.26(2) K) was observed.

From the viewpoints of molecular design and crystal engineering, the study on carboranyl biradicals should be important for the understanding of the physical character of paramagnetic carborane derivatives. There are large number of reports concerning the syntheses and physical properties of organic biradicals having various spin-coupling units.⁵ For instance, *o*-, *m*- and *p*-phenylenes are common π -conjugated aromatic spin-coupling units, and benzoquinodimethane (BQDM) radicals are shown in Chart 1(b). The molecular orbital (MO) theory predicts that only non-Kekulé



Chart 1

hydrocarbon *m*-BQDM has non-disjoint NBMOs, and the spin ground state will be a triplet while the other two isomers having disjoint MOs are expected to be singlet.^{6a} The valence bond (VB) theory by using the alternating spin-polarisation model is another approach for the qualitative understanding of the spin ground state. The VB theory also predicts that only *m*-BQDM is in high-spin ground state whereas *o*-, *p*-BQDMs are closed-shell molecules.^{6b} These theories well represent the spin ground states of the simple alternative hydrocarbon biradicals.

One of the unique characters of carboranes are their three-dimensional aromaticity.^{1d,7} The B-B and B-C bonds in

^aDepartment of Chemistry, The 21st Century COE Program, Aoyama Gakuin University, 5-10-1 Fuchinobe, Sagamihara, Kanagawa, 229-8558, Japan. E-mail: jiro_abe@chem.aoyama.ac.jp; Fax: +81 42 759 6225; Tel: +81 42 759 6225

^bCREST, Japan Science and Technology Agency, Kawaguchi Center Building, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan

^cDepartment of Applied Chemistry, Graduate School of Engineering, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo, 192-0397, Japan

^dDepartment of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-Aza-Aoba, Aoba-ku, Sendai, Miyagi, 980-8578, Japan

carboranes are non-classical, electron-deficient multi-centre bonds. Therefore carborane molecules have resonance energy resulting from the electron delocalisation as found in aromatic hydrocarbons. Taking advantage of the unique structure and the three-dimensional aromaticity, we propose a new series of the magnetic materials by use of carboranes. Herein we addressed our interest to the synthesis and investigation of the *ortho*-carboranyl bis(nitronyl nitroxide) derivative **OCB-BNN** (= 1",2"-bis(4'-phenylene(3,3,4,4-tetramethylimidazolyl-2-oxyl-5-oxide))-1",2"-dicarba-*closo*-dodecaborane; Chart 1(a); *ortho*-, R₁ = R₂ = NN) that can be considered as a prototype compound of this class of biradicals.

In this paper, the synthesis, structural and magnetic characterisation, and DFT calculation results of **OCB-BNN** will be described with the aim for the investigation of the character of the carborane cage as the building unit of the spin network.

Experimental

Preparation of OCB-BNN

OCB-BNN was synthesised from 1,2-bis(4'-formylphenyl)-1,2dicarba-*closo*-dodecaborane⁸ and 2,3-dimethyl-2,3-bis(hydroxylamino)butane, followed by oxidation using aqueous sodium *meta*periodide.^{5c}

To a methanol solution of 250 mg (0.709 mmol) of 1,2bis(4'-formylphenyl)-1,2-dicarba-*closo*-dodecaborane, 200 mg (1.35 mmol) of 2,3-dimethyl-2,3-bis(hydroxylamino)butane was added under nitrogen atmosphere at room temperature. The reaction mixture was continuously stirred for 10 days with exclusion of the light and the precipitate was filtered off. The short reaction time gave the mono-substituted derivative as the major product. The filtrate was washed with methanol and dried under reduced pressure. The radical precursor, 1",2"-bis(4'-phenyl(2,5dihydroxy-3,3,4,4-tetramethylimidazoly1))-1",2" -dicarba-*closo*dodecaborane was obtained as a white powder (375 mg, 86.3%).

The radical precursor (370 mg, 0.604 mmol) was oxidised in dichloromethane by excess of aqueous sodium *meta*-periodide at 0 °C under nitrogen. After 30 min, **OCB-BNN** was extracted with dichloromethane and the combined organic layer was dried over Na₂SO₄. After the solvent was removed under reduced pressure, the purification was performed using a column chromatograph packed with silica gel in Et₂O eluent. A blue powder of **OCB-BNN**·Et₂O (273 mg, 74.2%) was obtained. An X-ray-quality single crystal was prepared by the slow diffusion of diethyl ether into acetonitrile solution of **OCB-BNN**.

IR (KBr pellet): v_{max}/cm^{-1} 2593 (B–H) and 1368 (N–O). UV absorption: λ_{max}/nm (CH₂Cl₂) = 277 ($\varepsilon/dm^3 mol^{-1} cm^{-1}$ (26100), 285 (26000), 294 (26100), 377 (22500), 599 (580). The intense absorption band ascribed to the π - π^* transition band of nitroxides was observed below 400 nm. The weak and broad absorption band around 600 nm is attributable to the n– π^* transition of nitronyl nitroxides.

X-Ray crystallographic analysis

A blue block crystal of **OCB-BNN**·Et₂O ($C_{28}H_{42}B_{10}N_4O_4$ · (C_2H_5)₂O) having approximate dimensions of 0.20 × 0.10 × 0.10 mm³ was mounted on a glass fibre. All measurements were made on a Rigaku Saturn 70 CCD area detector with graphitemonochromated Mo-K α radiation; M = 680.89, monoclinic, space group $P2_1/c$ (no. 14), λ (Mo-K α) = 0.7107 Å, μ (Mo-K α) = 0.75 cm⁻¹, T = 123(1) K, a = 13.198(4), b = 21.760(5), c =13.410(4) Å, $\beta = 102.438(4)^\circ$, V = 3761.1(1) Å³, Z = 4, $D_c =$ 1.202 g cm⁻³.

Hydrogen atoms were located on the basis of geometrical consideration except B–H hydrogen atoms. All non-hydrogen atoms were refined anisotropically and the least-squares refinement (490 parameters) on 11054 independent reflections converged at $R_1(F) = 0.070$ (data for $I > 2.0\sigma(I)$), and $wR_2(F^2) = 0.149$ for all data; GOF = 1.009.

CCDC reference number 280804.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511579e

Magnetic measurements

The magnetic susceptibility at 0.1 T in the 2–300 K temperature range was carried out with a Quantum Design MPMS-XL SQUID magnetometer. The polycrystalline sample of **OCB-BNN** was contained in a diamagnetic gel-capsule.

The ESR signals of **OCB-BNN** in frozen toluene matrix were recorded on a JEOL JES-TE200 spectrometer operating at the X-band equipped with a digital temperature controller model 9650 (Scientific Instruments Inc.). Toluene was distilled on CaH_2 under nitrogen prior to use and the solution was degassed by the freeze–pump–thaw method.

Results and discussion

The molecular structure obtained by an X-ray crystallographic analysis is shown in Fig. 1(a). The bond lengths and angles are listed in Table 1 with the result of DFT calculation that will be described later.

All bond lengths and angles of **OCB-BNN** are reasonable as compared with those found in the literature. The leastsquare planes defined by O-N-C-N-O fragments of two nitronyl nitroxides lead to dihedral angles of 36.2(1) and 22.9(1)°,

Table 1 Selected bond lengths and angles. Calculated values were obtained from the DFT calculation (UB3LYP/ $6-31G^*$)

	Experimental	Calculated
Distances/Å		
N–O ^{•a}	1.285	1.275
$N-C(sp^2)^a$	1.359	1.365
C-C (phenylene) ^a	1.389	1.401
B-B ^a	1.775	1.778
$B-C^a$	1.721	1.717
C–C(carborane)	1.726	1.762
Angles/°		
	108.14	108.2
$O-N-C(sp^2)$	126.43	128.0
Dihedral, Ph-NN ^b	22.9	3.4^{c}
	36.2	

^{*a*} The mean length of the corresponding bonds. ^{*b*} Dihedral angles between the least square planes defined by O–N–C–N–O fragments of nitronyl nitroxide and phenylene rings. ^{*c*} The two dihedral angles were identical.



Fig. 1 (a) ORTEP drawing of **OCB-BNN** (50% probability). Et₂O molecules and geometrically calculated hydrogen atoms are omitted. (b) The molecular alignment in the crystal packing. Diethyl ether molecules are displayed by balls and sticks. (c) Intermolecular contacts along the *c*-axis. The intermolecular distances (Å) are as follows: a = 5.74, b = 3.85, c = 4.59, d = 5.13, e = 4.91, f = 3.70, g = 3.28, h = 4.07, i = 4.03, j = 5.54, k = 4.59, I = 4.91, m = 3.70, n = 3.40, o = 4.47.

respectively, for the mean planes using the benzene rings (C3–C8 and C16–C21). The shortest intramolecular oxygen–oxygen distance between nitronyl nitroxide fragments is 6.86(1) Å (O2–O4). On the one hand, the intermolecular contacts between

oxygen atoms $O1 \cdots^i O2$ and $O3 \cdots^i O4$ (symmetry operator (i) +x, -y + 1/2, z - 1/2) with distances of 4.592(3) and 4.911(3) Å are shorter than the intramolecular oxygen–oxygen distance, thereby forming a one-dimensional triangular column parallel to the crystallographic *c*-axis as shown in Fig. 1(b) and (c). From the crystallographic viewpoint, we note that the intramolecular magnetic interaction would not be predominant in the solid state by comparison with the intermolecular interaction.

A theoretical calculation was carried out in order to obtain insight into the electronic ground state of OCB-BNN. Unfortunately, the SCF single-point energy calculation at the B3LYP/6-31G* level for the isolated OCB-BNN itself using the experimental geometry could not converge because the experimental structure might be far from the theoretical equilibrium structure. The detailed results for the DFT calculation have been reported in our previous paper.9 The geometry optimisations were carried out at the unrestricted B3LYP level of the theory using the 6-31G* basis set, and converged to identical structures in singlet and triplet states. The calculated bond lengths and angles are listed in Table 1. The dihedral angles of the least-square mean-planes of two radical fragments (O-N-C-N-O) with respect to benzene rings are optimised as 3.4° by the DFT calculation, while the experimental angles are 36.2(1) and $22.9(1)^{\circ}$. This difference might arise from the steric hindrance of diethyl ether in the crystal lattice. The energy levels of singlet and triplet states were also calculated. The spinsquared expectation value $\langle S^2 \rangle$ after spin projections are calculated as $\langle S^2 \rangle_{\text{singlet}} = 1.04$ and $\langle S^2 \rangle_{\text{triplet}} = 2.01$, respectively. The large spin eigenvalue of the singlet state indicates the spin contamination of the wavefunction from higher spin states. Similarly to other nitroxides in the literature, most spin population is located on the O-N-C-N-O part and the spin distributions on the benzene ring and carborane cage are small.10 The total energies are obtained as $E_{\text{singlet}} = -1860.6229193$ Hartree for the singlet and $E_{\text{triplet}} =$ -1860.6229177 Hartree for the triplet state. The singlet-triplet energy gap ($\Delta E_{\text{s-T}} = E_{\text{singlet}} - E_{\text{triplet}}$) was 1.6 \times 10⁻⁶ Hartree. The intramolecular magnetic exchange interaction was estimated for the spin Hamiltonian defined as $H = -2J_{calc}S_1 \cdot S_2$ according to the literature method.¹¹ The calculated energy difference of **OCB-BNN** corresponds to the exchange interaction of $2J_{calc}/k_{\rm B} =$ -0.53 K predicting a weak antiferromagnetic interaction between the nitronyl nitroxides.

The magnetic susceptibility of the polycrystalline sample was measured by a SQUID magnetometer (Fig. 2). The temperature dependence of the magnetic susceptibility was measured under 0.1 T of applied magnetic field.

At 300 K, the $\chi_m T$ value was 0.777 emu K mol⁻¹, slightly higher than the theoretical value for two moles of S = 1/2 radicals. The $\chi_m T$ value was constant in the temperature range between 300 and 100 K, then began to decrease gradually below 100 K and showed abrupt decreasing in lower temperature. This fact indicates the presence of antiferromagnetic interaction in the solid state. The reciprocal susceptibility was fitted by the Curie–Weiss law with parameters C = 0.781(6) emu K mol⁻¹ and $\theta = -1.05(4)$ K between 10 and 300 K. The obtained Curie constant corresponds to twice the isolated S = 1/2 value and the negative Weiss constant indicates a weak short-range antiferromagnetic interaction in the crystal.¹²

The ESR spectrum in toluene solution shows nine lines of hyperfine structure which corresponds to four equivalent nitrogen



Fig. 2 $\chi_m T vs. T$ plot (\Box) and Curie–Weiss plot (\bigcirc) with theoretical fitting (solid line) for **OCB-BNN**.

atoms at room temperature. The hyperfine coupling constant (a_N) is 0.363 mT (= 2.4×10^{-4} K) which is comparable with those of the nitronyl nitroxide family having four equivalent nitrogen nuclei in the literature.^{5c} This ESR spectrum means that the intramolecular magnetic exchange interaction (J_{ESR}/k_B) is significantly larger than the hyperfine coupling constant ($|J_{ESR}/k_B| \gg a_N$). The variable-temperature ESR spectra of **OCB-BNN** in frozen toluene matrix (9.6 × 10^{-6} mol dm⁻³) were measured in order to evaluate the intramolecular magnetic interaction with exclusion of intermolecular interaction. The ESR signal intensities (= I_{ESR}) were obtained by using double integration of the first-derivative spectra. The temperature dependence of the $I_{ESR}T$ product is shown in Fig. 3.



Fig. 3 Temperature dependence of $I_{ESR}T$ in frozen toluene matrix. The solid curve shows the fitting result described in the text.

At liquid-helium temperature, a very weak ESR signal indicating an antiferromagnetic intramolecular coupling was observed, and no half-field signal around g = 4 was found. The $I_{\text{ESR}}T$ data was fitted by the modified Bleaney–Bowers equation (eqn (1); where C' is a fitting coefficient) for the Hamiltonian $H = -2J_{\text{ESR}}S_1 \cdot S_2$,¹³ giving the antiferromagnetic interaction $J_{\text{ESR}}/k_{\text{B}} = -27(2)$ K. The calculated curve is shown in Fig. 3.

$$I_{\rm ESR}T = \frac{C'}{3 + \exp(-2J_{\rm ESR}/k_{\rm B}T)}\tag{1}$$

A larger exchange interaction was observed for the isolated molecule in frozen matrix, whereas the Weiss constant of the crystalline state is smaller. This difference probably arises from the structural difference in both states. In the crystalline state, diamagnetic molecules, *i.e.* diethyl ether is interposed between nitronyl nitroxide arms, and the magnetic centres are separated by approximately 7 Å. On the other hand, in solution, diethyl ether would be released into bulk solution and the two nitroxide arms are allowed to rotate around the C6–C9 and C19–C22 bonds. The rotation of the imidazole rings might induce the proximity of the nitroxides that increases the dipolar interaction. The magnetic interaction between spin sites provides the most important insights for our goal of understanding the magnetic exchange through a carborane cage.

Taking into account the results of X-ray crystallography, ESR and DFT studies, the antiferromagnetic interaction should be a through-space dipole interaction among radicals. It is obvious that the phenylene rings between the radical and carborane cage impair the intramolecular exchange interaction through a carborane cage. However, initial attempts to synthesise a radical without chemical coupler gave unsatisfactory results because of poor stability of the target compound, and the synthesis is continuously under investigation. More progressive researches and syntheses of other analogues are also now in progress.

Conclusion

In summary, we have demonstrated here the first example of a carboranyl biradical molecule, **OCB-BNN**. The ESR measurement in frozen matrix evaluated the intermolecular magnetic interaction as -27(2) K.

Our magnetic measurement revealed the spin ground state of **OCB-BNN** is a singlet, and the DFT calculation that predicts the singlet spin ground state is consistent with the experimental results. This result gave insights on the physical properties of the paramagnetic carborane family. In this case, we can conclude that *o*-carborane framework having nitronyl nitroxide radicals exhibits intramolecular antiferromagnetic interaction.

Acknowledgements

This work was partly supported by a Grant-in-Aid for young scientists B (No. 16750125) from the MEXT, Japan. F. I. and M. Y. thank the Japan Science and Technology Agency (JST) for financial support. F. I. and J. A. are grateful for financial support of the 21st Century COE program of Aoyama Gakuin University.

References

1 (a) Z. Xie, Acc. Chem. Res., 2003, 36, 1; (b) R. N. Grimes, Angew. Chem., Int. Ed., 2003, 42, 1198; (c) S. O. Kang and J. Ko, Adv. Organomet. *Chem.*, 2001, **47**, 61; (*d*) R. B. King, *Chem. Rev.*, 2001, **105**, 1119; (*e*) V. I. Bregadze, *Chem. Rev.*, 1992, **92**, 209; (*f*) J. Plesek, *Chem. Rev.*, 1992, **92**, 269; (*g*) L. A. Leites, *Chem. Rev.*, 1992, **92**, 279, and references therein.

- 2 (a) M. F. Issac and S. B. Kahl, J. Organomet. Chem., 2003, 680, 232; (b) J. Johnsamuel, Y. Byun, T. P. Jones, Y. Endo and W. Tjarks, J. Organomet. Chem., 2003, 680, 223; (c) I. B. Sivaev, S. Sjoberg and V. I. Bregadze, J. Organomet. Chem., 2003, 680, 106; (d) J. F. Valliant, K. J. Guenther, A. S. King, P. Morel, P. Schaffer, O. O. Sogbein and K. A. Stephenson, Coord. Chem. Rev., 2002, 232, 173; (e) A. Maderna, R. Huertas, M. F. Hawthorne, R. Luguya and M. G. H. Vicent, Chem. Commun., 2002, 1784; (f) J. F. Valiant, O. O. Sogbein, P. Morel, P. Schaffer, K. J. Guenther and A. D. Bain, Inorg. Chem., 2002, 41, 2731.
- 3 (a) M. G. H. Vicent, S. J. Shetty, A. Wickramasinghe and K. M. Smith, *Tetrahedron Lett.*, 2000, **41**, 7623; (b) H. Nemoto, J. G. Wilson, H. Nakamura and Y. Yamamoto, J. Org. Chem., 1992, **57**, 435.
- 4 F. Iwahori, K. Kamibayashi, Y. Nishikawa, M. Yamashita and J. Abe, *Chem. Lett.*, 2004, **11**, 1460.
- 5 For example;(a) A. Rajca, Chem. Rev., 1994, 94, 871; (b) D. A. Shultz, A. K. Boal, H. Lee and G. T. Farmer, J. Org. Chem., 1999, 64, 4386; (c) the following papers especially deal with bis-nitronylnitroxide radicals: E. F. Ullman, J. H. Osiecki, D. G. B. Boocock and R. Darcy, J. Am. Chem. Soc., 1972, 94, 7049; (d) M. Tanaka, K. Matsuda, T. Itoh and H. Iwamura, Angew. Chem., Int. Ed., 1998, 37, 810; (e) L. Catala, J. L. Moigne, N. Kyritsakas, P. Rey, J. J. Novoa and P. Turek, Chem. Eur. J., 2001, 11, 2466.
- 6 (a) W. T. Borden and E. R. Davidson, J. Am. Chem. Soc., 1977, 99, 4587; (b) A. A. Obchinnikov, Theor. Chim. Acta, 1978, 47, 297.

- 7 P. v. R. Schleyer and K. Najafian, *Inorg. Chem.*, 1998, **37**, 3454; J. Aihara, *J. Am. Chem. Soc.*, 1978, **100**, 3339.
- 8 1,2-Bis(4'-formylphenyl)-1,2-dicarba-*closo*-dodecaborane was synthesised from 4,4'-bis(2*H*-1,3-dithiolane)diphenylacetylene and decaborane ($B_{10}H_{14}$) followed by the cleavage reaction of the protective groups by Hg(ClO₄)₂-6H₂O. The mercury(II) perchlorate is explosive and it should be handled carefully.
- 9 Proceedings of the Conference on the Science and Technology of Synthetic Metals: F. Iwahori, K. Kamibayashi, K. Mori, Y. Nishikawa, M. Yamashita and J. Abe, *Synth. Met.*, 2005, in press.
- 10 Y. Pontillon, T. Akita, A. Grand, K. Kobayashi, E. Lelievre-Berna, J. Pécaut, E. Ressouche and J. Schweizer, *J. Am. Chem. Soc.*, 1999, **121**, 10126; A. Zheldev, V. Barone, M. Bonnet, B. Delley, D. Grand, E. Ressouche, P. Rey, R. Subra and J. Schweizer, *J. Am. Chem. Soc.*, 1994, **116**, 2019.
- 11 K. Yamaguchi, Y. Takahara and T. Fueno, *Applied Quantum Chemistry*, ed. V. H. Smith, *et al.*, 1986, p. 155.
- 12 Because of the comparable intra- and intermolecular contact distances between the radicals, the data fitting by a singlet-triplet two-spin model based on the molecular structure is insufficient to obtain physically meaningful parameters for the crystalline sample. Tentative treatment by using the modified Bleaney–Bowers equation (ref. 11) gave $J_{cryst}/k_B = -1.59(1)$ K and $zJ_{cryst}'/k_B = -0.33(1)$ K, where J_{cryst}/k_B means a predominant intradimer magnetic interaction and zJ_{cryst}'/k_B describes interdimer magnetic interaction by the mean field approximation (C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29**, 203).
- 13 B. Bleaney and K. D. Bowers, Proc. R. Soc. London, Ser. A, 1952, 214, 451.