408 *Inorg. Chem.* **1999,** *38,* 408−410

Molecular Structure, Conformational Analysis, and Electronic Spectra of 1-Phenyl-1-aza-*closo*-dodecaborane(12)

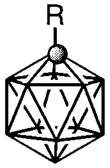
Wolfgang Fendrich,[†] **James E. Harvey, and Piotr Kaszynski***

Organic Materials Research Group,
Department of Chemistry, Vanderbilt University,
Nashville, Tennessee 37235

Received June 26, 1998

Introduction

In our pursuit of *closo*-boranes as structural elements for liquid crystalline materials,[1−6] we considered 1-aza-*closo*-dodecaborane(12) (**1a**) as a candidate for materials with a high dipole moment and mesogens with a large dielectric anisotropy.[1,4] Such materials are essential electrooptical components for most nematic-based liquid crystal displays.[7]



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a, R = H
b, R = Me
c, R = C_6H_5
d, R = C_6H_4-4-OBu
e, R = C_6H_4-4-Br

A typical calamitic liquid crystalline molecule requires an elongated molecular shape[8,9] which can be achieved in **1a** by placing substituents in the 1 and 12 positions of the cage. A recently described preparation of N-substituted[10−12] derivatives of azadodecaborane and selective iodination of 1-methyl-1-aza-*closo*-dodecaborane(12) (**1b**) in the 12 position[13] have opened the synthetic possibility of incorporating **1a** into structures of typical liquid crystalline molecules.

Here we provide a detailed analysis of 1-phenyl-1-aza-*closo*-dodecaborane(12)[11] (**1c**) and assessment of **1a** as a building block for liquid crystalline materials. We report ab initio molecular geometry and conformational analysis of **1c**, electronic spectra in relation to its electronic structure, and its chemical reactivity.

Results and Discussion

Synthesis of **1c** was accomplished according to the literature procedure[11] in 10% overall yield based on decaborane(14). The last step in the synthesis, a borane insertion reaction, turned out to be particularly moisture and oxygen sensitive and was carried out in a drybox. The procedure appears to be general and has been adopted for preparation of the 4-butoxyphenyl (**1d**) and 4-bromophenyl (**1e**) derivatives, which were obtained in about 10% overall yields.[14]

Aryl derivatives **1c**−**1e** are white solids which melt at 123, 87, and 151 °C, respectively. They show moderate sensitivity to moisture, which is consistent with the report of facile reactions of **1** with strong nucleophiles leading to the formation of cage-opened nido products.[11,15] Phenyl derivative **1c** is transfromed completely in moist benzene within 24 h, although no appreciable reaction is detected during the first 2 h. Addition of methanol (10% v/v) to the benzene solution results in fast solvolysis of **1c** as evident from ^{11}B NMR spectra[14] and in accord with previous reports of similar reactions.[15] Slow reaction is observed in carefully dried acetonitrile (about 40% after 4 h) based on the ^{11}B and UV spectra. This results from the tendency of azadodecaborane to reduce the coordination number at the N-atom.

The solvolysis products were not isolated. Their ^{11}B and ^{1}H NMR spectra and also UV spectra are consistent with the nido structures expected for the product resulting from nucleophilic cage opening of aza-*closo*-dodecaborane.[11]

The molecular geometry of **1c** was optimized for its eclipsed (**1c-E**) and staggered (**1c-S**) conformers at the HF/6-31G* level of theory with C_s symmetry constraints (Figure 1). According to the calculations, both conformers exhibit a similar N−C_{Ph} distance of 1.483 and 1.482 Å (XRD for **1e**,[16] 1.46(5) Å), and the phenyl group is slightly tilted with respect to the cage molecular axis ($\alpha_{C(4)-N-B(12)} = 178.1°$). The presence of the phenyl substituent results in equal widening of the B−N distance in both conformers (1.741 Å avg) as compared to the parent 1-aza-*closo*-dodecaborane **1a** (calculated, 1.710 Å: GED,[17] 1.716(9) Å). At the same time the calculated average B_2−B_3 distance in both conformers is shorter by 0.005 Å than that in the parent (calculated, 1.821 Å; GED,[17] 1.825(6) Å).

The calculations favor the eclipsed conformer **1c-E** (Figure 2), while the staggered form **1c-S** represents a transition state on the potential energy hypersurface, based on normal-mode analysis. The gas phase thermodynamic stability of **1c-E** is consistent with the conformational preference of the phenyl ring lying on a crystallographically imposed mirror plane observed

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[†] A visiting student from the V. Vill group at Hamburg University.

(1) Kaszynski, P.; Huang, J.; Jenkins, G. S.; Bairamov, K. A.; Lipiak, D. *Mol. Cryst. Liq. Cryst.* **1995**, *260*, 315.

(2) Kaszynski, P.; Lipiak, D. In *Materials for Optical Limiting*; MRS Symposium Proceedings 374; Crane, R., Lewis, K., Stryland, E. V., Khoshnevisan, M., Eds.; Materials Research Society: Pittsburgh, PA, 1995; p 341.

(3) Douglass, A. G.; Czuprynski, K.; Mierzwa, M.; Kaszynski, P. *Chem. Mater.* **1998**, *10*, 2399.

(4) Kaszynski, P.; Lipiak, D.; Bairamov, K. A.; Brady, E.; Patel, M. K.; Laska, J. In *Advances in Boron Chemistry*; Siebert, W., Ed.; The Royal Society of Chemistry: Bodmin, Cornwall, U.K., 1997; pp 507−513.

(5) Czuprynski, K.; Douglass, A. G.; Kaszynski, P.; Drzewinski, W. *Liq. Cryst.* **1999**, *26*, 261.

(6) Douglass, A. G.; Czuprynski, K.; Mierzwa, M.; Kaszynski, P. *J. Mater. Chem.* **1998**, *8*, 2391.

(7) Sage, I. In *Thermotropic Liquid Crystals*; Gray, G. W., Ed.; Wiley: New York, 1987; pp 64−73 and references therein.

(8) Demus, D. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 54.

(9) Collings, P. J.; Hird, M. *Introduction to Liquid Crystals Chemistry and Physics*; Taylor & Francis: Bristol, U.K., 1997.

(10) Meyer, F.; Muller, J.; Schmidt, M. U.; Paetzold, P. *Inorg. Chem.* **1993**, *32*, 5053.

(11) Lomme, P.; Meyer, F.; Englert, U.; Paetzold, P. *Chem. Ber.* **1995**, *128*, 1225.

(12) Paetzold, P. *Eur. J. Inorg. Chem.* **1998**, 143.

(13) Lomme, P.; Roth, M.; Englert, U.; Paetzold, P. *Chem. Ber.* **1996**, *129*, 1227.

(14) Described in Supporting Information.

(15) Meyer, F.; Muller, J.; Paetzold, P.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1227.

(16) Crystal data for **1e** at 20 °C: $C_6H_{15}B_{11}BrN$, $M = 300.01$, orthorhombic, space group *Pnma* (No. 62), $a = 18.95(3)$ Å, $b = 7.24(2)$ Å, $c = 10.21(4)$ Å, $Z = 4$, μ(Cu Kα) = 37.4 cm^{-1}, $R(F) = 0.137$; $R_w(F) = 0.163$ for 525 reflections with $I > 3.0\sigma(I)$. Despite the poor quality of the available crystals and the high residuals, the space group determination was unambiguous. The Br atom, phenyl ring, and azaborane cage were located on a crystallographically imposed mirror plane.

(17) Hnyk, D.; Buhl, M.; Schleyer, P. v. R.; Volden, H. V.; Gundersen, S.; Muller, J.; Paetzold, P. *Inorg. Chem.* **1993**, *32*, 2442.

10.1021/ic980737d CCC: $18.00

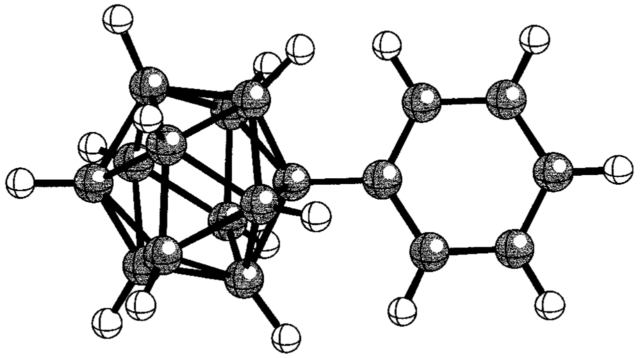

Figure 1. Optimized (HF/6-31G*) eclipsed molecular structure of 1-phenyl-1-aza-*closo*-dodecaborane (**1c**-**E**).

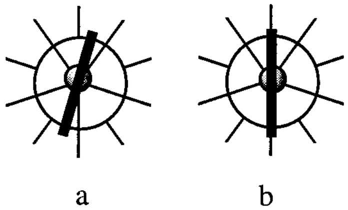

Figure 2. Extended Newman projection along the long molecular axes for staggered (a) and eclipsed (b) conformations of 1-phenyl-1-aza-*closo*-dodecaborane (**1c**). The bar represents the phenyl substituent plane.

in a single crystal of **1e**.[16] Such a comparison, however, is unreliable. In contrast to the calculations, the phenyl group in the solid structure of the isoelectronic Ph-$B_{12}H_{11}(-2)$ adopts an almost ideal staggered conformation with respect to the cage.[18]

The calculated (HF/6-31G*) enthalpy and free energy differences between the eclipsed and staggered conformers of **1c** (Figure 2) are $\Delta H^{\ddagger}_{298} = 0.58$ kcal/mol and $\Delta G^{\ddagger}_{298} = 1.92$ kcal/mol. These energy differences are almost identical to those calculated for the isoelectronic 1-phenyl-*p*-carborane and Ph-$B_{12}H_{11}(-2)$ which also prefer the eclipsed over the staggered conformation.[14] The calculated $H_{Ph}\cdots H_B$ close contacts in **1c**-**E** are 1.935 and 2.231 Å, while in **1c**-**S** these distances are slightly more favorable at 2.008 and 2.648 Å. In the staggered form, however, cage hydrogen atoms induce ring puckering (1.6°), which appears to be less favorable than ring tilting in the eclipsed conformer.

The phenyl derivative **1c** has the electronic state $^1A'$ and its HOMO (−9.86 eV; A″) and the LUMO (2.46 eV; A″) are shown in Figure 3. While the HOMO and most high-lying occupied MO's are localized either on the ring or on the cage, the LUMO and several lower-lying occupied MO's (e.g. HOMO-10) extend over the phenyl ring and the cage. This indicates some electronic interactions between the two fragments, which is supported by the electronic absorption spectrum of **1c** shown in Figure 4.

The UV spectrum of **1c** consists of three bands at 262 nm (log $\epsilon = 2.2$), 219 nm (log $\epsilon = 3.74$), and 193 nm (log $\epsilon = 4.33$), and it closely resembles that of benzene and its derivatives monosubstituted with auxochromes.[19] The two benzene absorption bands, B and E_2 are red-shifted in **1c** by 1130 and 3330 cm^{-1}, respectively (Figure 4). The magnitude of the E_2 band shift is greater than that observed in toluene[19] and anilinium cation,[19] and is similar to that in chlorobenzene[19] and methyl phenyl sulfone.[20] Clearly the electronic structure of the nitrogen atom in **1c** is different from that in aniline and anilinium cation. According to the natural bond orbital[21] analysis, the N atom forms the exocyclic bond to the phenyl carbon in **1c** using an $sp^{2.3}$ hybrid. For the endo-cyclic bonding of the N atom to the boron atoms of the upper belt the nitrogen uses two $sp^{4.5}$ and one $sp^{1.9}$ hybrids.

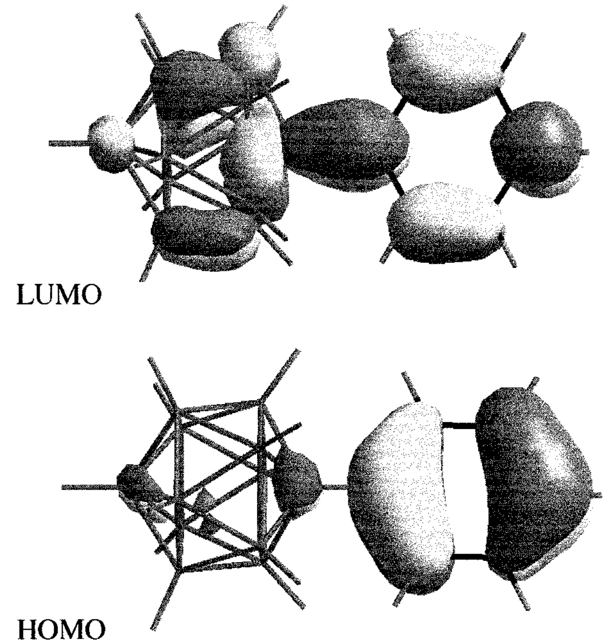

Figure 3. Representation of the HOMO (−9.86 eV; A″) and the LUMO (2.46 eV; A″) of **1c**-**E**.

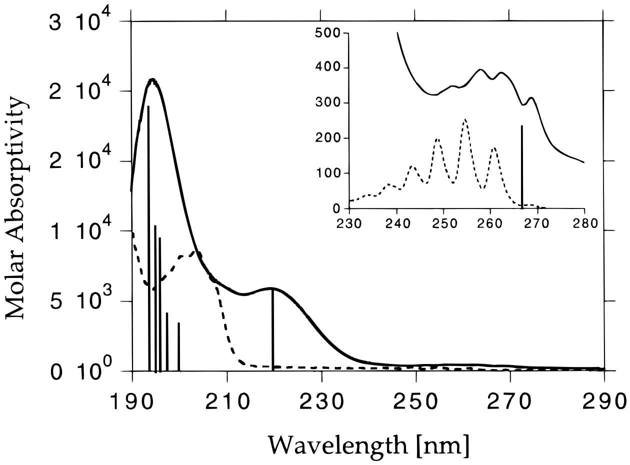

Figure 4. Absorption spectrum for 1-phenyl-1-aza-*closo*-dodecaborane (**1c**) (solid line) and benzene (dashed line) recorded in *n*-hexane. Inset shows the B band area. Vertical lines represent the ZINDO calculated major transitions scaled by 3.2 × 104. The calculated transition shown in the inset is exaggerated 10-fold.

The benzenoid origin of the absorption bands and the absence of charge-transfer (CT) transitions in **1c** have been confirmed with ZINDO//HF/6-31G* calculations.[22] The calculated transition energies and the corresponding relative oscillator strength

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[18] Peymann, T.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1998**, *37*, 1544.

[19] DMS: *UV Atlas of Organic Compounds*; Plenum Press: New York, 1966.

[20] Bychkova, T. I.; Vasileva, M. A.; Kalabina, A. V.; Rozova, T. I.; Ratovskii, G. V. *Russ. J. Org. Chem.* **1984**, *20*, 473.

[21] Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO*, Version 3.1.

[22] ZINDO calculations were performed in the Cerius^2 3.5 suite of programs.

values are shown in Figure 4 as vertical lines. According to the calculations all high intensity (>5% relative) transitions above 200 nm involve intra-ring electronic transitions, while the absorption at 193 nm is composed mostly of intra-cage (196–197 nm) and ring-to-cage transitions (195 nm).

Ab inito calculations (HF/6-31G*) show that the intracage B–N polarization in the parent azaborane **1a** results in a substantial dipole moment of 4.67 D,[23] which is comparable to that of biphenyl-1-carbonitrile (4.34 D),[24] an important structural element for liquid crystalline materials. Upon substitution of the nitrogen atom with a phenyl group in **1c**, the dipole moment increases to 6.39 D, according to HF/6-31G* calculations.

Cage iodination of **1c** or **1d** at the 12 position proved difficult. Reaction of I_2 or IBr in the presence of $AlCl_3$ in CH_2Cl_2 or hexane and under the conditions used for iodination of **1b**,[13] failed to produce the expected 12-iodo derivatives based on NMR spectra. Attempts at iodination with ICl in CH_2Cl_2 were inconclusive.[14]

A variety of 1-aryl-1-aza-*closo*-dodecaboranes can be prepared by adaptation of the literature method.[11] The electronic absorption spectrum of **1c** shows that the azaborane cage only slightly perturbs the arene spectrum above 200 nm and the ring-to-cage CT bands lie below 200 nm, according to ZINDO calculations. Ab initio calculations indicate a high dipole moment for **1c**. Relatively low UV absorption combined with a significant dipole moment make **1c** attractive for use in liquid crystal materials. The major drawback is the solvolytic instability and difficulties with functionalization of the azaborane cage. In addition, the pronounced sensitivity to nucleophiles will make it difficult to find suitable conditions for a successful cross-coupling reaction of iodoazaboranes. Finally, the calculated low activation energy for the intramolecular rotation around the cage-ring bond in **1c** is similar to that found for 1-phenyl-*p*-carborane. Even though the latter has been successfully used as a structural element for liquid crystals,[5] low interconversion barriers are expected to decrease the thermal stability of the liquid crystal phases.[25]

Acknowledgment. This project has been supported in part by the NSF Career Grant (DMR-9703002). We are grateful to Dr. James G. Carver of Redstone Arsenal for a generous gift of decaborane and to Prof. Timothy P. Hanusa for assistance with X-ray crystallography.

Supporting Information Available: Listing of crystal data, data collection, solution and refinement, anisotropic thermal parameters, bond distances, chemical procedures for the preparation of aryl derivatives of 1-aza-*closo*-dodecaborane, their attempted iodination reactions, and reactions with solvents are available (10 pages). Ordering information is given on any current masthead page.

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(23) Zahradnik, R.; Balaji, V.; Michl, J. *J. Comput. Chem.* **1991**, *12*, 1147.

(24) Cumper, C. W. N.; Dev, S. K.; Landor, S. R. *J. Chem. Soc., Perkin Trans. 2* **1973**, 537.

(25) Kaszynski, P.; Czuprynski, K. *Liq. Cryst.*, submitted.