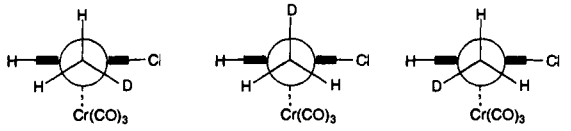


Figure 1. Newman projections down the C(a)-C(aromatic) bond of the three different conformations of the methyl group.

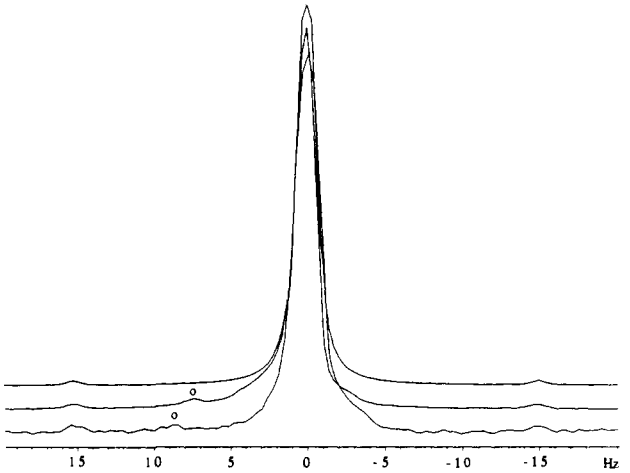
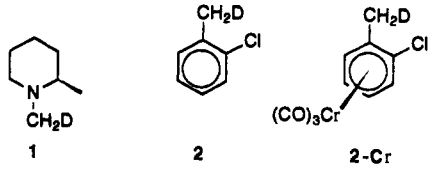


Figure 2. Deuterium-coupled ^{1}H NMR spectra of the CH_2D AB pattern in **2-Cr**-d_1. Top: Simulated spectrum fit to the 500-MHz spectrum (J = 14.7 Hz, $\Delta\nu$ = 4 Hz, w = 1 Hz). Middle: 500-MHz spectrum. Bottom: 600-MHz spectrum. o = Trace of unlabeled **2-Cr**.

hypothesis for the magnitude of the diastereotopicity in **1** is correct, then it should be possible to detect the chirotopicity of a methyl group in a compound like (α-deuterio-o-chlorotoluene)chromium tricarbonyl (**2-Cr**) (Figure 1).



1 **2** **2-Cr**

Reduction of α-bromo-o-chlorotoluene with lithium aluminum deuteride in tetrahydrofuran yields α-deuterio-o-chlorotoluene (**2**).[10] Treatment of **2** with chromium hexacarbonyl in refluxing diglyme affords **2-Cr**.[11,12]

A cursory glance at the ^{1}H NMR spectrum of **2-Cr** at 500 MHz in benzene-d_6 shows the expected aromatic signals (7.0-8.0 ppm) and a 1:1:1 triplet for the methylene protons (2.5 ppm, $J_{H,D}$ = 2.2 Hz). A closer look betrays two additional triplets, one to either side of the central peak but of minuscule (1-2%) intensity. Deuterium decoupling collapses the central peaks into a singlet, and the wing signals follow suit (Figure 2). The spectrum at 600 MHz shows a similar behavior, whereas spectra at 360 or 300 MHz shows no wings at all. The spectra at 500 and 600 MHz are invariant to changes in spinning rate and are reproduced in samples of different concentrations and synthetic batches.

Under conditions where the ratio of the AB coupling constant to the chemical shift difference between sites A and B, $\Delta\nu$(AB), is large, a second-order three-line AB pattern can appear.[13] There is a specific relationship between the differences of the chemical shifts of the signals and the relative intensities of the lines in the spectrum. From one set plus the coupling constant one can obtain the other. The expected range of $\Delta\nu$(AB) in order to observe a three-line pattern with $J_{H,H}$ ca. 15 Hz lies between 2 and 5 Hz; the intensity of the wings compared to the central peak ranges between 1 and 3%.

The spectrum of **2-Cr** shows these general features. From the deuterium-coupled spectra were derive the value for the geminal H,H coupilng ($J_{H,D}$ = 2.2 Hz, $J_{H,H}$ = 14.7 Hz). With this coupling and the measured $\Delta\nu$ between the wings (30.0 Hz), we can simulate the spectrum for various $\Delta\nu$(AB). Figure 2 shows the best fit to the spectrum at 500 MHz, $\Delta\nu$(AB) = ca. 4.0 Hz. To our knowledge, **2-Cr** is the first example of a second-order AB pattern resulting from isotopic substitution at a chirotopic methyl group.

This study demonstrates the power of NMR spectroscopy to elucidate even subtle aspects of molecular symmetry. It also opens up the possibility of designing new reagents for determining the configuration at stereogenic methyl groups (a la Anet et al.[14]) by direct NMR observations.

Acknowledgment. We thank the National Science Foundation Presidential Young Investigator Award Program (CHE-8857812), the American Cancer Society Junior Faculty Fellowship Program (C-58024), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We greatly appreciate additional support of our program from the Exxon Educational Fund, Hofman-La Roche, Rohm+Haas, Monsanto, Eli Lilly, Zambon (Italia), and Sterling Drug. The 500-MHz NMR spectrometer was purchased with funds from NIH (RR04733) and NSF (CHE-8814866). We thank Dan Iverson (Varian) for the 600-MHz spectra.

(10) Spectral data for **2**: bp 158-159 °C (ca. 95% yield); ^{1}H NMR ($CDCl_3$) δ 2.36 (t, 2 H, J_{HD} = 2.1 Hz), 7.18 (m, 2 H), 7.28 (dd, 1 H, J = 6.83 Hz, J = 1.9 Hz), 7.40 (dd, 1 H, J = 6.82 Hz, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 19.7 (t), 126.6 (d), 127.1 (d), 129.0 (d), 130.8 (d), 134.3 (s), 135.9 (s).

(11) Spectral data for **2-Cr**: mp 99-101 °C (lit. mp 101-102 °C) (ca. 38% yield); ^{1}H NMR ($CDCl_3$) δ 2.32 (t, 2 H, J_{HD} = 2.1 Hz), 5.10 (td, 1 H, J = 6.23 Hz, J = 1.1 Hz), 5.22 (td, 1 H, J = 6.23 Hz, J = 1.1 Hz), 5.32 (dd, 1 H, J = 6.23 Hz, J = 1.1 Hz), 5.55 (dd, 1 H, J = 6.23 Hz, J = 1.1 Hz); ^{13}C NMR ($CDCl_3$) δ 19.1 (t), 90.3 (d), 90.8 (d), 93.1 (d), 93.6 (d), 106.1 (s), 111.7 (s), 231.9 (s).

(12) Unlabeled **2-Cr** has been prepared: Fukiu, M.; Endo, Y.; Oishi, T. *Chem. Pharm. Bull.* **1980**, *28*, 3639.

(13) Reference 2, pp 150-158.

(14) Anet, F. A. L.; O'Leary, D. J.; Beale, J. M.; Floss, H. G. *J. Am. Chem. Soc.* **1989**, *111*, 8935.

The Rigidity of Sucrose: Just an Illusion?

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The conformation of sucrose in solution has been under scrutiny by NMR spectroscopic and theoretical studies for over ten years.[1] Early NMR and HSEA modeling studies concluded that the molecule exists in solution in a single conformation similar to its crystal structure.[2] These findings were supported by detailed ^{13}C relaxation measurements.[3a-d] However, a recent NOE study[1] and molecular mechanics calculations[4a,b] indicate that sucrose in solution is flexible.

Up to now, the solution conformation of sucrose was determined on the basis of just one[2] or two[1] interglycosidic NOE contacts. We sought to extend this data base by conducting more detailed NMR experiments on sucrose in aqueous solution. Table I lists interglycosidic NOE contacts obtained for sucrose in D_2O and

(1) Hervé du Penthoat, C.; Imberty, A.; Roques, N.; Michon, V.; Mentech, J.; Descotes, G.; Pérez, S. *J. Am. Chem. Soc.* **1991**, *113*, 3720-3727, and references therein.

(2) Bock, K.; Lemieux, R. U. *Carbohydr. Res.* **1982**, *100*, 63-74.

(3) (a) McCain, D. C.; Markley, J. L. *J. Am. Chem. soc.* **1986**, *108*, 4259-4264. (b) McCain, D. C.; Markley, J. L. *Carbohydr. Res.* **1986**, *152*, 73-80. (c) McCain, D. C.; Markley, J. L. *J. Magn. Reson.* **1987**, *73*, 244-251. (d) Kovacs, H.; Bagley, S.; Kowalewski, J. *J. Magn. Reson.* **1989**, *85*, 530-541.

(4) (a) Tran, V. H.; Brady, J. W. *Biopolymers* **1990**, *29*, 961-976. (b) Tran, V. H.; Brady, J. W. *Biopolymers* **1990**, *29*, 977-997.

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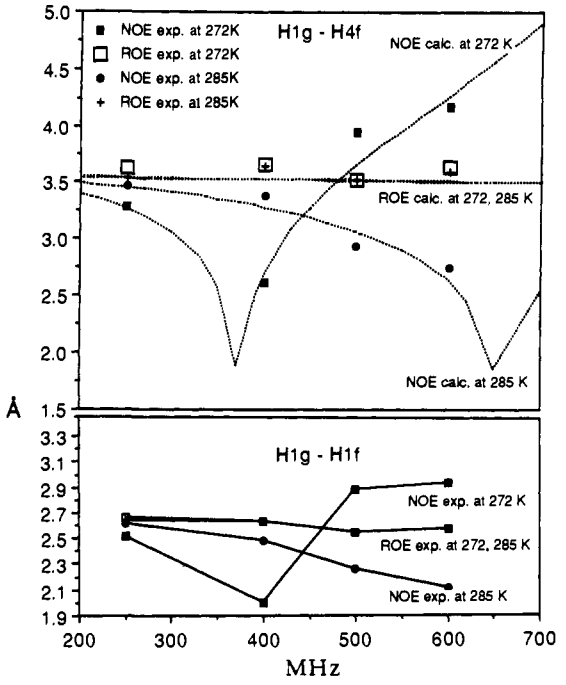

Figure 1. Results from 1D NOESY[7a,b] and 1D ROESY[8a,b] measurements on sucrose in H_2O solution at two different temperatures and four magnetic field strengths obtained on Bruker AM-250, AMX-400, AM-500, and AMX-600 spectrometers. The pulse sequences utilized composite 90° selective excitation[9] (t_{90} = 10 ms) at the H1g resonance. For the duration of the entire experiment, the carrier frequency remained at the H1g resonance. The effective spin-lock field was set between 0.9 and 1.7 kHz to minimize Hartmann–Hahn effects.[10] The spectra were recorded for up to 11 different mixing times ranging from 0.03 to 1.1 s for the NOESY experiments and from 0.03 to 0.3 s for the ROESY experiments. The relaxation delay and acquisition times were 1.1 and 1.6 s, respectively; 160 or 320 scans were accumulated per spectrum. All experiments were repeated twice. Cross-relaxation rates were obtained by linear extrapolation of $[I_{ij}(\tau_m)/I_{ii}(\tau_m)]/\tau_m$ vs τ_m to zero mixing time,[11] where I_{ij} and I_{ii} are the intensities of the NOE-enhanced and the selectively excited signals, respectively. Rotating-frame cross-relaxation rates were corrected[10] for offset of the j-resonance from the carrier frequency. Laboratory-frame and rotating-frame NOE distances, $r^{\parallel,\perp}_{app}$(H1g–H4f) and $r^{\parallel,\perp}_{app}$(H1g–H1f), were calculated from $(\sigma^{\parallel,\perp}(\text{H1g–H2g})/\sigma^{\parallel,\perp}(\text{H1g–H4f}))^{1/6} r_{\text{H1g–H2g}}$ and $(\sigma^{\parallel,\perp}(\text{H1g–H2g})/0.5\sigma^{\parallel,\perp}(\text{H1g–H1'f}))^{1/6} r_{\text{H1g–H2g}}$, respectively, where $r_{\text{H1g–H2g}}$ was set to 2.4 Å. Standard errors calculated with the error propagation are 1–2.5%. Theoretical values for $r_{\text{H1g–H4f}}$ are drawn with dotted lines.

H_2O solutions.[5] Additionally, ROESY experiments revealed a single chemical exchange,[6] namely, between the OH2g and OH1f proton pair, reminiscent of OH2g···OH1f hydrogen bonding as it occurs in the crystalline state.[2] All NOE-derived distances compiled in Table I are compatible with a single solution conformation; they do not differ strongly from the corresponding distances observed in the crystal structure. This conclusion also agrees with the ^{13}C relaxation studies,[3a–d] which might lead us, at first glance, to conclude that sucrose is tumbling as a rigid body in aqueous solution.

If, however, the glycosidic bond in sucrose were rigid, we should observe neither temperature- nor magnetic field-dependence of the interglycosidic proton–proton distances derived from NOE measurements. To verify this, and thus the apparent rigidity of the sucrose molecule, we quantified the easily accessible interresidue dipolar interactions between H1g and H1f, between H1g and H4f, and, as a reference, the intraresidue NOE between H1g and H2g, within a large dispersion range, i.e., for a number of temperatures and magnetic field strengths, spanning $0.16 < \omega\tau_c < 3.0$. The results are presented in Figure 1 in the form of

(5) Sucrose (5 mg) was dissolved in 0.5 mL of D_2O–$(CD_3)_2CO$, 6:1, v/v, or H_2O–$(CD_3)_2CO$, 6:1, v/v, at neutral pH.

(6) Davis, D. G.; Bax, A. *J. Magn. Reson.* **1985**, *64*, 533–535.

Table I. Apparent Interproton Distances Derived from Interglycosidic NOE Contacts for Sucrose in Aqueous Solution

proton pair[a]	distance[b] [Å]	proton pair[a]	distance[b] [Å]
H1g–H1f	2.6	H1g–OH1f	3.6
H1g–H3f	3.5	H1g–OH6f	3.4
H1g–H4f	4.6	H1g–OH3f	4.0
H1g–H6f	4.0	H1f–OH2g	3.2
H5g–H4f	3.0	H5g–OH3f	3.8

[a] Data for aliphatic protons were acquired at 300 K, those for hydroxyl protons at 263 K, on a Bruker AM-500 spectrometer; *g* stands for glucosyl, *f* for fructosyl ring. [b] Distances were calculated from the formula

$$r_{ij} = (\sigma_{ref}/\sigma_{ij})^{1/6} r_{ref}$$

where σ_{ref} and r_{ref} are the cross-relaxation rate and the distance of the reference pair of protons. The precision of the distances is estimated at $0.1 \times r$. As reference distances, we used H1g–H2g = 2.4 Å, H1g–H3g = 3.7 Å, and H1g–H4g = 4.0 Å.

apparent distances $r^{\parallel}_{app}$ and $r^{\perp}_{app}$ obtained from laboratory frame ($\sigma^{\parallel}$) and rotating frame ($\sigma^{\perp}$) cross-relaxation rates, respectively.[12] Indeed, $r^{\parallel,\perp}_{app}$(H1g–H2g) was found to be 2.5 ± 0.04 Å and showed neither temperature- nor magnetic field-dependence over the trajectories investigated, pointing to overall isotropic motion of sucrose in solution.[13] However, the strong variations observed for the two interglycosidic $r^{\parallel}_{app}$ values with temperature and magnetic field strength (see Figure 1) suggest that some fast intramolecular rearrangement must occur. The experimental data obtained in the present study cannot be explained in terms of fructofuranose ring puckering alone[3a,d] or by the anisotropy of molecular tumbling.[3d] The first process is too fast[14] to cause temperature- and field-dependence of spectral densities,[3a,d] and the overall motion appeared virtually isotropic from the analysis of H1g–H2g cross-relaxation rates and from ^{13}C T_1 data.[3a–d]

To gain further insight into the intramolecular dynamics of sucrose, we calculated the theoretical temperature- and field-dependence for $r^{\parallel,\perp}_{app}$(H1g–H4f) by applying a simplified model;[15]

(7) (a) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546–4553. (b) Williamson, M. P.; Neuhaus, D. *J. Magn. Reson.* **1987**, *72*, 369–375.

(8) Bothner-By, A. A.; Stephens, R. L.; Lee, J.; Warren, C. D.; Jeanloz, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 811–813. (b) Bax, A.; Davis, D. G. *J. Magn. Reson.* **1985**, *63*, 207–213.

(9) Sklenar, V.; Feigon, J. *J. Am. Chem. Soc.* **1990**, *112*, 5664–5666.

(10) Bax, A. *J. Magn. Reson.* **1988**, *77*, 134–147.

(11) Macura, S.; Farmer II, B. T.; Brown, L. R. *J. Magn. Reson.* **1986**, *70*, 493–499.

(12) The apparent interglycosidic distances were calculated from the formulas:

$$r^{\parallel}_{app} = \left(\frac{|6J_2 - J_0|}{|6J^{iso}_2 - J^{iso}_0|}\right)^{1/6} \text{ and } r^{\perp}_{app} = \left(\frac{3J_1 + 2J_0}{3J^{iso}_1 + 2J^{iso}_0}\right)^{1/6}$$

where J_n are the spectral densities derived from the model, $J^{iso}_n = \tau_0/1 + (n\omega\tau_0)^2$ are the spectral densities for isotropic motion with correlation time τ_0, and ω is the ^1H resonance frequency of the spectrometer. For the H1g–H2g interaction

$$r^{\parallel}_{app} = \left[\frac{5.69 \times 10^{10}}{\sigma^{\parallel}}(6J^{iso}_2 - J^{iso}_0)\right]^{1/6} = r^{\perp}_{app} = \left[\frac{5.69 \times 10^{10}}{\sigma^{\perp}}(3J^{iso}_1 + 2J^{iso}_0)\right]^{1/6}$$

where τ_0 was obtained from the ratio $\sigma^{\parallel}/\sigma^{\perp}$ obtained for each temperature and magnetic field as proposed: Davis, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 3471–3472.

(13) The apparent lengthening of the H1g–H2g distance as compared with the crystal value of 2.409 Å obtained from the neutral diffraction study (Brown, G. M.; Levy, H. A. *Acta Crystallogr.* **1973**, *B29*, 790–797) may be caused by local, small-amplitude vibrational, and torsional motions.[3a,d]

(14) Lister, D. G.; MacDonald, J. N.; Owen, N. L. *Internal Rotation and Inversion*; Academic Press: New York, 1978.

the input parameters were estimated by comparing the theoretical results obtained by a rough grid search[16] to experimental data. The results of our model calculations, included in Figure 1, suggest that large variations in interglycosidic torsional angles are responsible for the observed variation of $r_{app}^{\parallel}$ for both the H1g-H4f and H1g-H1f interactions. It is important to note that the NOE-derived distances measured in this study do not correspond to statistical averages, as it often assumed[1,17] but to the motionally averaged values.[18a-e]

In summary, we have conclusively demonstrated the internal flexibility of sucrose in solution from interresidual, laboratory-frame cross-relaxation rates ($\sigma^{\parallel}$), a parameter that gives unique information about intramolecular dynamics.[18a,19a-d,20] In contrast, rotating-frame cross-relaxation rates as well as intraresidual, laboratory-frame cross-relaxation rates, like ^{13}C relaxation times,[3a-d] appeared virtually insensitive to this type of internal motion for a fast-tumbling molecule in solution. Paradoxically, it appeared that, for $\omega\tau_c \sim 1$, interresidue cross-relaxation rates measured from the *laboratory* frame of reference reflected *internal* molecular motions, i.e., they gave insight into a frame of reference corresponding to the viewpoint of an individual molecule.

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Registry No. Sucrose, 57-50-1.

Supplementary Material Available: ^1H NMR spectra (including 1D ROESY and 1D double-selective TOCSY-ROESY) of sucrose in H_2O (3 pages). Ordering information is given on any current masthead page.

(15) For the calculations of spectral densities we assumed that sucrose tumbles isotropically, each unit is rigid, and the molecule changes its conformations by jumps around the glycosidic bond that are decoupled from the overall motion and can be described by a single correlation time, τ_i. In this case spectral density functions have a simple form (Lipari, G.; Szabo, A. *J. Am. Chem. Soc.* **1982**, *104*, 4546-4559):

$$J_n = \tilde{S}^2 \frac{\tau_0}{1 + (n\omega\tau_0)^2} + (\langle r^{-6} \rangle - \tilde{S}^2) \frac{\tau}{1 + (n\omega\tau)^2}$$

$$\text{where } \tilde{S}^2 = \sum_{m=-2}^{m=2} \left| \left\langle \frac{Y_{2m}(\Omega)}{r^3} \right\rangle \right|^2$$

$Y_{2m}(\Omega)$ are spherical harmonics functions with r and Ω corresponding to the distance and polar angle of a given proton pair in the molecular frame, $\langle \cdots \rangle$ denotes ensemble average, and $\tau^{-1} = \tau_0^{-1} + \tau_i^{-1}$. More elaborate models can be found: Tropp, J. *J. Chem. Phys.* **1980**, *72*, 6035-6043. Baldo, M.; Grassi, A.; Perly, B. *Mol. Phys.* **1988**, *64*, 51-63.

(16) Based on previous results[4a,b] we assumed that sucrose flips among three minimum energy conformations in (Φ, Ψ) space: A = (-5°, -50°), B = (-20°, -170°), and C = (17°, 50°) obtained after a few steps of MM2 energy minimization. Φ = H1g-C1g-O1-C2f and Ψ = C1g-O1-C2f-O5f. We assumed that overall and internal motions are thermally activated processes[3d] having the form

$$\tau_{0,i} = A_{0,i} \exp\left(\frac{E_{0,i}}{RT}\right)$$

R is the gas constant, T is temperature, and $A_{0,i}$ and $E_{0,i}$ are adjustable parameters. For the H1g-H4f interaction measured in the temperature range from 263 to 330 K at 500 MHz, and at two temperatures (272 and 285 K) at four different magnetic fields (250, 400, 500, and 600 MHz), we obtained the following set of parameters: populations (p_A, p_B, p_C) = (0.38, 0.38, 0.24), distances (r_A, r_B, r_C) = (4.0, 4.0, 2.1 Å), $\tilde{S}^2$ = 0.000425, E_0 = 28 kJ/mol, A_0 = 2 fs, E_i = 16 kJ/mol, A_i = 11 fs. Almost the same parameters E_0 and A_0 were obtained from the temperature dependence of τ_0 calculated from cross-relaxation rates for the H1g-H2g proton pair.

(17) Cumming, D. A.; Carver, J. P. *Biochemistry* **1987**, *26*, 6664-6676.

(18) (a) Tropp, J. *J. Chem. Res.* **1980**, *72*, 6035-6043. (b) Olejniczak, E. T.; Dobson, C. M.; Karplus, M.; Levy, R. M. *J. Am. Chem. Soc.* **1984**, *106*, 1923-1930. (c) Kessler, H.; Griesinger, C.; Müller, A.; Van Gunsteren, W. F.; Berendsen, H. J. C. *J. Am. Chem. Soc.* **1988**, *110*, 3393-3396. (d) LeMaster, D. M.; Kay, L. E.; Brunger, A. T.; Prestegard, J. H. *FEBS Lett.* **1988**, *236*, 71-76. (e) Koning, T. M. G.; Boelens, R.; Kaptein, R. *J. Magn. Reson.* **1990**, *90*, 111-123.

(19) (a) Farmer II, B. T.; Macura, S.; Brown, L. R. *J. Magn. Reson.* **1988**, *80*, 1-22. (b) Lane, A. N.; Lefèvre, J. F.; Jardetzky, O. *J. Magn. Reson.* **1986**, *66*, 201-218. (c) Elbayed, K.; Canet, D.; Brondeau, J. *Mol. Phys.* **1989**, *68*, 295-314. (d) Duben, A. J.; Hutton, W. C. *J. Am. Chem. Soc.* **1990**, *112*, 5917-5929.

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3-Carboranylcarbene: A Boron-Substituted Carbene[1]

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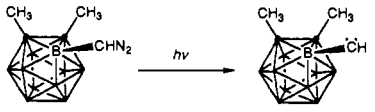
The chemistry of carbenes substituted with electron-donating groups is an old and rich one, with all manner of substituents well explored.[2] The chemistry of carbenes substituted with electropositive elements is so far restricted to theoretical studies. In particular, there is no example of a boron-substituted carbene outside of a computer. Only a few potential precursors are known,[3] although some beautiful new diazo compounds have recently been made by the group of Bertrand.[4] Here we describe the synthesis of 1,2-dimethyl-3-(diazomethyl)-*o*-carborane (**1**) and the first reactions of the carbene derived from it, **2**.



1 2

In these figures the dots represent carbons and all other vertices are borons. There is a hydrogen at each unoccupied vertex. The boron shown as a "B" is at the 3 position.

Boron-substituted carbenes have received substantial theoretical attention and are species of considerable interest. As with many carbenes, an issue of importance is the presence of two low-lying spin states, the singlet and triplet. In simple species such as H_2B-CH, the boron acts to stabilize the singlet state through overlap of its empty 2p orbital with the filled orbital of the carbene containing the two nonbonding electrons. At the same time, the relatively electropositive boron atom acts through the σ system to stabilize the triplet. Calculations agree that this balancing act yields a pair of spin states quite close in energy.[5] In the case of **2**, in which there is not expected to be good connection between extracage and cage orbitals,[6] it is as if the singlet stabilization had been turned off. Accordingly, one might expect enhanced triplet activity.

Tosylhydrazone **3** was made by insertion of a vinyl-substituted boron into $Li_2B_9C_2H_{11}$,[7] methylation of the two cage carbons, ozonolysis, and reaction with tosylhydrazine. Heating the sodium salt under vacuum (120 °C/0.02 Torr) led to the diazo compound

(1) Support from the National Science Foundation through Grant CHE-90-24996 is gratefully acknowledged.

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(4) Arthur, M.-P.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1991**, *113*, 5856.

(5) For summaries, see: Davidson, E. R. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982. Moss, R. A.; Jones, M., Jr. *React. Intermed. (Wiley)* **1985**, *3*, 45. For recent calculations as well as a summary of earlier work, see: Schleyer, P. v. R.; Luke, B. T.; Pople, J. A. *Organometallics* **1987**, *6*, 1997. Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270.

(6) Hutton, R. S.; Roth, H. D.; Chari, S. *J. Phys. Chem.* **1981**, *85*, 753.

(7) Hawthorne, M. F.; Young, D. C.; Garrett, P. M.; Owen, D. A.; Schwerin, S. G.; Tebbe, F. N.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 862.

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