Study of Ion Pair Solution Structure Using Nuclear Overhauser Effects: Interionic $^1H\{^1H\}$ and $^{11}B\{^1H\}$ Nuclear Overhauser Effects in the $(CH_3CH_2CH_2CH_2)_4N^+,BH_4^-$ Ion Pair

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Phase-transfer reactions between anions and neutral species are often catalyzed by lipophilic cations. It has been shown that the cation's structure can influence the rates and stereochemistry of phase-transfer reactions,[1,2] making the rational design of cationic phase-transfer catalysts a reasonable approach to obtaining substrate specificity and product selectivity. Toward this goal, we have begun an investigation of the structure and dynamics of the phase-transfer species, the ion pair formed by reagent anion and lipophilic cation. In particular, we wished to determine whether interionic nuclear Overhauser effects (NOEs) might be observed, and if so, whether they are specific and informative concerning ion-pair structure. We now show that the tetrahydroborate anion (BH_4^-), often used as a reagent in phase-transfer reductions, is a useful NMR probe for such studies, as ^1H and ^{11}B ($I = {}^3/_2$) are both magnetically active nuclei. ^{11}B nuclear relaxation is typically dominated by quadrupolar mechanisms, and the dipolar relaxation responsible for the NOE can be observed only if the electric field gradient at the ^{11}B nucleus is 0 or small.[3-5] This condition appears to be satisfied for the $(CH_3CH_2CH_2CH_2)_4N^+,BH_4^-$ ion pair in $CDCl_3$. We now describe the observation of specific $^1H\{^1H\}$ and $^{11}B\{^1H\}$ NOEs on the BH_4^- anion upon selective saturation of the proton resonances of the $(CH_3CH_2CH_2CH_2)_4N^+$ ion in $CDCl_3$ solution.[6]

Steady-state $^1H\{^1H\}$ and $^{11}B\{^1H\}$ NOE difference spectra (Figure 1) were obtained upon saturation of the alkyl ^1H resonances of the cation. The NOE observed from the α-CH_2 protons to the BH_4^- protons (18.0%) is slightly greater than double that observed from the β-CH_2 protons to the BH_4^- protons (8.1%) (Greek letters refer to labels in Figure 2). Smaller but nonnegligible NOEs were also observed upon saturation of the γ-CH_2 (3.5%) and δ-CH_3 (1.0%) protons. NOEs show little or no concentration dependence over a range of 0.02–0.6 M, indicating that aggregation, if present, does not significantly affect the observed NOE in this concentration range, although a slight (0.23 ppm from 0.02 to 0.6 M) upfield shift of the BH_4^- resonance lines occurs with increasing concentration. A temperature dependence of the NOE is seen; NOEs decrease with decreasing temperature. However, it is not clear from present data whether this temperature dependence is due solely to changes in solvent viscosity or if aggregation is contributing to an increase in correlation time. This is being investigated presently. *In all cases, the ratio of NOEs to the BH_4^- protons upon saturation of the α-CH_2 protons remains roughly double that observed from the β-CH_2 protons.* We interpret this observation to mean that the observed NOEs reflect the structure of the tight ion pair, regardless of the state of aggregation.

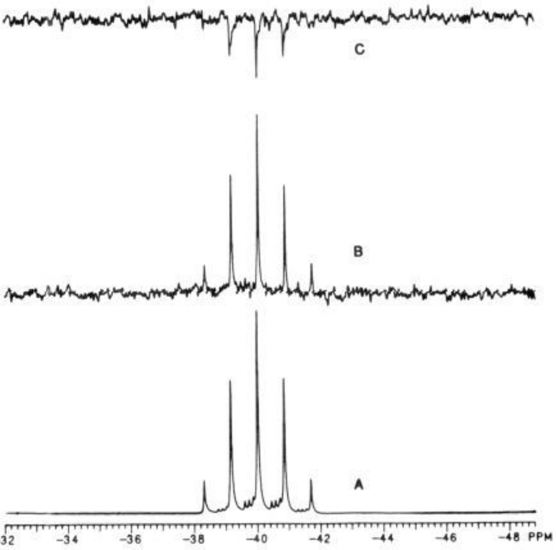

Figure 1. (A) The 96.23-MHz ^{11}B spectrum of **1** (0.2 M in $CDCl_3$, 25 °C). Note the presence of a quartet of triplets, somewhat offset by an isotope effect, due to the presence of some BH_3D^-. (B) $^{11}B\{^1H\}$ NOE difference spectrum obtained upon subtraction of a spectrum obtained with off-resonance saturation from one in which the α-CH_2 proton resonances were saturated for 12.5 s prior to acquisition. Integration indicates a 2.1% NOE enhancement of the ^{11}B signal. (C) Same as for spectrum B except that the β-CH_2 signal was saturated. Integration indicates a −0.8% NOE on the ^{11}B nucleus. Spectra B and C are plotted to the same scale.

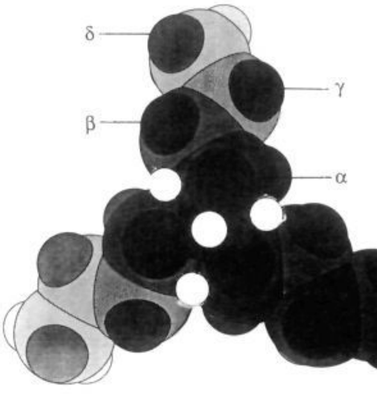

Figure 2. Proposed model of equilibrium structure for the $(CH_3CH_2CH_2CH_2)_4N^+,BH_4^-$ ion pair. See text for explanation. For clarity, a ball-and-stick model is used to represent the BH_4^-, while the $(CH_3CH_2CH_2CH_2)_4N^+$ ion is represented by a space filling model.

The ^{11}B (96.23 MHz) spectrum of the ion pair (Figure 1) shows the expected 1:4:6:4:1 quintet ($^1J_{HB}$ = 81 Hz). The measured T_1 of the ^{11}B nucleus (T_1 = 2.5 s, 294 K, 0.2 M in $CDCl_3$)[7] indicates substantial suppression of quadrupolar relaxation.[8] The NOEs to ^{11}B are small but reproducible: saturation of the α-CH_2 protons of the cation gives rise to a positive (2.1%) NOE at boron, while saturation of the β-CH_2 protons give rise to a negative (−0.8%) $^{11}B\{^1H\}$ NOE.[9] The large $^1H\{^1H\}$ NOEs observed on

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[1] Julia, S.; Ginebreda, A.; Guixer, J.; Masana, J.; Tomas, A.; Colonna, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 574.

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[3] Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect: Chemical Applications*; Academic Press: New York, 1971.

[4] Wehrli, F. W. *Annual Review of NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: New York, 1979; Vol. 9, pp 126–220.

[5] Specific $^6Li\{^1H\}$ NOEs have been recently reported in organolithium complexes. See: Hoffmann, D.; Bauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1990**, 208–211. We note that because ^6Li has a very small quadrupolar moment, observation of the $^6Li\{^1H\}$ NOE is not restricted to sites with zero electric field gradient.

[6] All spectra were obtained on a Varian XL-300 spectrometer operating at 300 MHz (^1H) using a broad-band probe. Samples for NOE and T_1 experiments were freeze–thaw degassed prior to the experiment to remove dissolved oxygen. Fresh samples were prepared for each run. Reagent grade $(CH_3CH_2CH_2CH_2)_4N^+,BH_4^-$ was purchased from Aldrich and used without further purification. $CDCl_3$ was deacidified prior to sample preparation by passage through neutral activated alumina. NOE-enhanced spectra were obtained by selective saturation on-resonance for 10 s ($^1H\{^1H\}$) or 12.5 ($^{11}B\{^1H\}$), followed by acquisition with the decoupler turned off. Reference spectra were obtained in the same manner with the decoupler set to an empty region of the spectrum. Spectra were obtained in an interleaved fashion at 25 °C. ^1H spectra are referenced to the residual $CHCl_3$ line. ^{11}B spectra are referenced to external $BF\cdot Et_2O$ in $CDCl_3$.

[7] ^{11}B T_1 values were measured by using a standard inversion–recovery pulse sequence (delay–π–τ–$\pi/2$–acquire). Five τ values were used, with a recovery delay of 20 s.

[8] Seidle, A. R. *Annual Review of NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: New York, 1982; Vol. 12, pp 177–257.

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the BH_4^- protons by saturation of the same resonances should produce a substantial indirect (negative) NOE at boron, and it is the difference between the positive (direct) and negative (indirect) effects that is observed. Evidently, direct effects predominate at the ^{11}B nucleus upon saturation of the α-CH_2 protons, while the indirect effects predominate upon saturation of the β-CH_2.

These results indicate a close equilibrium association between the BH_4^- anion and the quaternary nitrogen, a result at odds with some predictions.[10] Figure 2 shows a model for the ion-pair structure which rationalizes the observed NOEs. This model places each of three BH_4^- hydrogens in van der Waals contact with two α-CH_2 protons and one β-CH_2 proton in a pyramidal site created by three *n*-butyl side chains and the quaternary nitrogen. The α-CH_2 and β-CH_2 groups of each *n*-butyl group are in staggered (anti) conformation, and a C_3 symmetry axis through the nitrogen and the C-α carbon of the fourth *n*-butyl side chain (not shown) is present. This packing arrangement optimizes Coulombic interaction, with CPK models indicating a N–B distance of ca. 3 Å (M–B distances in crystalline alkali tetrahydroborates range from 2.5 to 3.7 Å).[10] The van der Waals contact with two α-CH_2 protons and one β-CH_2 proton for each of three BH_4^- hydrogens rationalizes the experimental ratio of NOEs to the BH_4^- protons of ca. 2:1 obtained upon saturation of the α-CH_2 and β-CH_2 protons, respectively. The predominance of the indirect (negative) NOE to the ^{11}B nucleus upon saturation of the β-CH_2 protons is also reasonable on the basis of this model, since the BH_4^- protons are on a time average directly between the β-CH_2 protons and the boron nucleus.

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(9) For comparison, we note that 12.5-s broad-band ^1H presaturation of all proton resonances gives rise to a 30.0% $^{11}B\{^1H\}$ NOE in the same sample. A more complete description of the $^{11}B\{^1H\}$ NOE, which to our knowledge has not been previously reported, is in progress.

(10) Weber, W. P.; Gokel, G. W. *Phase Transfer Catalysis in Organic Synthesis*; Springer-Verlag: Berlin, 1977; p 15.

(11) Greenwood, N. N. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., et al., Eds.; Pergamon Press, New York, 1971; Chapter 11, p 746.

Hexafluorobenzene Oxide and Hexafluorooxepin

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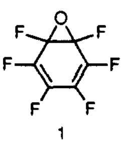
An elegant study by Vogel[1,2] revealed benzene oxide and oxepin to be a rapidly equilibrating pair of valence isomers with interesting spectroscopic properties and reactivity. We now report the synthesis of hexafluorobenzene oxide (**1**) and describe some of its chemistry, including the relationship with its valence isomer hexafluorooxepin (**2**).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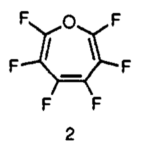
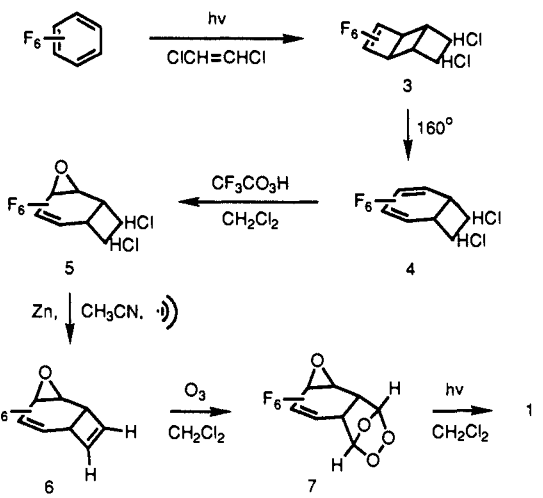

2

Scheme I



Earlier unavailing attempts in England[3] and in our laboratory[4] to prepare these compounds persuaded us that our quarry was very sensitive. We therefore designed a synthetic approach (Scheme I) culminating in a photoreaction that could be carried out in an inert medium in the cold.

Photocycloaddition of 1,2-dichloroethylene to hexafluorobenzene yielded a stereoisomeric mixture of *anti*-tricyclo[4.2.0.0^{2,5}]oct-3-enes (**3**) which were readily separable into cis and trans fractions by distillation.[5] Heating these at 160 °C gave bicyclic dienes *endo*-**4c** and **4t**, respectively. Each diene was epoxidized with peroxytrifluoroacetic acid[4] to yield, respectively, tricyclic oxiranes *endo*-**5c** and **5t**. Ultrasound-assisted dechlorination of the oxiranes with zinc gave the delicate diene **6** in low yield. Ozonation of **6** produced an endo/exo mixture of ozonides **7**, which was irradiated at $\lambda > 280$ nm.[6] Bulb-to-bulb distillation of the rather complex product mixture gave in addition to solvent a single volatile compound.

Its mass spectrum displayed a parent peak at m/e 202 for C_6F_6O, together with fragment peaks corresponding to loss of O, CO, CO + F, and CO + CF_2 (base, $C_4F_4^+$). The ^{19}F NMR spectrum (CH_2Cl_2) comprised three signals of equal area at 149.2, 152.8, and 154.3,[7] a finding consistent with the hexafluorobenzene oxide but not the hexafluorooxepin structure. Signal assignments, shown below, are based on comparison with model cyclohexadienes and on variable temperature NMR behavior to be discussed. Note that the fluorines geminal to oxygen appear ~60 ppm upfield from their expected position in the oxepin, as judged from model compounds **8** and **9**.[8] The presence of a fluorinated oxirane ring was indicated by an IR band at 1445 cm^{-1}.[9] A UV maximum at 246 nm (ϵ = 7400, s-C_6H_{12}) confirmed the presence of the cyclohexadiene chromophore.

While solutions of **1** in typical nonpolar solvents were found to be quite stable at room temperature, the benzene oxide rearranges spontaneously and cleanly to hexafluorocyclohexa-2,4-

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(2) For a review, see: Vogel, E.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 385.

(3) Barlow, M. G.; Haszeldine, R. N.; Peck, C. J. *J. Chem. Soc., Chem. Commun.* **1980**, 158.

(4) Dailey, W. P.; Ralli, P.; Wasserman, D.; Lemal, D. M. *J. Org. Chem.* **1989**, *54*, 5516.

(5) For other examples of haloolefin photocycloadditions to hexafluorobenzene, see: (a) Roberts, B. E.; Goldman, G. D.; Lemal, D. M. *J. Fluorine Chem.*, in press. (b) Barefoot, A. C., III; Saunders, W. D.; Buzby, J. M.; Grayston, M. W.; Lemal, D. M. *J. Org. Chem.* **1980**, *45*, 4292. (c) Lemal, D. M.; Buzby, J. M.; Barefoot, A. C., III; Grayston, M. W.; Laganis, E. L. *J. Org. Chem.* **1980**, *45*, 3118. (d) Rahman, M. M.; Secor, B. A.; Morgan, K. M.; Shafer, P. R.; Lemal, D. M. *J. Am. Chem. Soc.*, in press.

(6) Developed by Story, the photolysis of ozonides has been reviewed by Adam: Adam, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *86*, 638.

(7) ^{19}F NMR chemical shifts are reported in parts per million upfield from internal trichlorofluoromethane.

(8) Toy, M. S.; Stringham, R. S. *J. Org. Chem.* **1979**, *44*, 2813. Toy, M. S.; Stringham, R. S. *J. Fluorine Chem.* **1978**, *12*, 23.

(9) Fluorinated epoxides typically absorb at somewhat higher frequencies; diene epoxide **6**, for example, has a band at 1495 cm^{-1}.

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