Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1994, **4(6)**, 221–223
Mendeleev Communications

Synthesis and Dynamic Properties of Cyclooctatetraenyl(dipropyl)borane

Mikhail E. Gurskii,[a] Ilya D. Gridnev,[a] Alexei V. Buevich,[a] Tamara V. Potapova,[a] Vadim I. Mstislavsky,[a] Anatoly O. Krasavin[b] and Yurii N. Bubnov*[a]

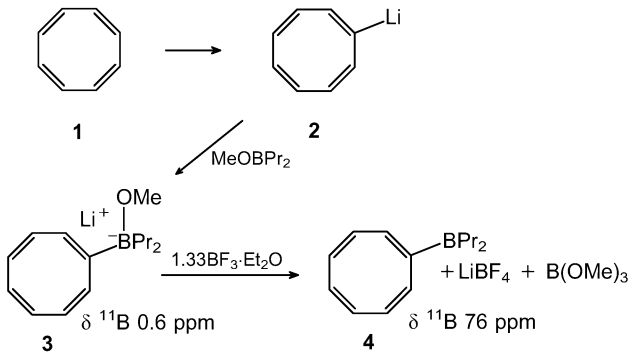
[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation. Fax: +7 095 135 5328*
[b] *Higher Chemical College of the Russian Academy of Sciences, 125820 Moscow, Russian Federation.*

Cyclooctatetraenyldipropylborane **4** has been synthesized in 47% yield; activation parameters for bond shifting in **4** determined by lineshape analysis of the ^{13}C NMR spectra are $\Delta G^{\ddagger}(298) = 67.7\pm0.1$ kJ mol^{-1}; $\Delta H^{\ddagger} = 58.1\pm0.8$ kJ mol^{-1}; $\Delta S^{\ddagger} = -32\pm5$ kJ mol^{-1} K^{-1}.

For the last 83 years, since it was first synthesized, cyclooctatetraene[1] has been the object of extensive investigations.[2,3] This compound is a central point in the solution of many fundamental problems of chemistry, *i.e.* aromaticity and anti-aromaticity, valent tautomerism, dynamic stereochemistry, *etc.* Moreover, cyclooctatetraene has proved to possess great synthetic potential; use of **1** as a classic ligand in the synthetic chemistry of transition metals clusters,[2] as a starting compound in the synthesis of various polyunsaturated molecules and macrocycles,[2] or as a building block for obtaining stereoregular polyacetylenes[4] can be mentioned.

In the course of our study of polyunsaturated organo-

boranes[5] and NMR studies of the dynamic behaviour of allylic-type boron derivatives[6] we have prepared cyclooctatetraenyl(dipropyl)borane **4** by the reaction of lithium cyclooctatetraenide[7] with methoxy(dipropyl)borane followed by treatment of the ate-complex **3** formed with boron trifluoride etherate (yield 47%):



Target compound **4**† was isolated by vacuum distillation; its ^{1}H NMR spectrum is shown in Fig. 1. Signal assignments in the ^{1}H and ^{13}C NMR spectra of **4** were made using standard ^{1}H–^{1}H COSY and ^{1}H–^{13}C correlation experiments. Freshly-obtained borane **4** is a dark yellow oil, which is stable below 0 °C, but prolonged storage at room temperature or heating at 100 °C for several hours leads to irreversible changes in the NMR spectra of **4**.

Similarly to all vinylboranes, compound **4** is very sensitive to protolytic reagents, and gives **1** on treatment with acetic acid.

As with all other cyclooctatetraenes, compound **4** exibits fluxional behaviour due to a reversible bond shift in its tetraene system.[3] The 2D ^{13}C EXSY spectrum of **4** indicating the exchange pathway in this compound is shown in Fig. 2.

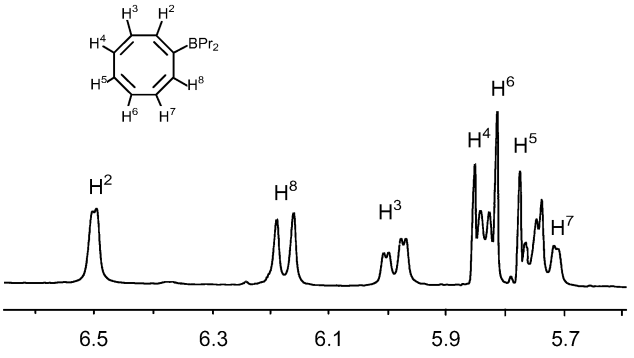


Fig. 1 Section plot of the ^{1}H NMR spectrum (400 MHz, 25 °C, [^{2}H$_8$]toluene) of cyclooctatetraenyl(dipropyl)borane **4**. Spectral lines are broadened due to reversible bond shifting.

† *Synthesis of* **4**: Pr_2BOMe (5.8 g, 45.3 mmol) was added to a solution of lithium cyclooctatetraenide[7] in ether at −78 °C and the reaction mixture was heated to room temperature. It was then stirred for 2 h, again cooled to −78 °C and $BF_3{\cdot}OEt_2$ (7.44 ml, 60 mmol) was added. After being heated to room temperature the resulting precipitate was filtered off and solvents were removed *in vacuo*. The residue was distilled to give 4.3 g (47%) of **4**, b.p. 72–73 °C (8×10^{-2} mmHg), n_D^{20} 1.5109. Found: C 84.28, H 10.52, B 4.64. Calc. for $C_{14}H_{21}B$: C 84.02, H 10.58, B 5.40%. Parameters for the NMR spectra of **4** are given in Table 1.

Coupling constants were extracted from a double quantum phase sensitive COSY spectrum which was clear enough to obtain couplings with an accuracy of about 0.3 Hz.

Lineshape analysis was carried out following the approach described in, ref. 9, *i.e.* by direct iterative search of $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ from the whole set of experimental spectra. Signals from all the exchanging carbon atoms were used in calculations except for the signal of C^2. The latter was excluded due to rather high temperature dependence of the chemical shift (> 1 Hz K^{-1}). 1024 points were used for digitizing of each spectrum.

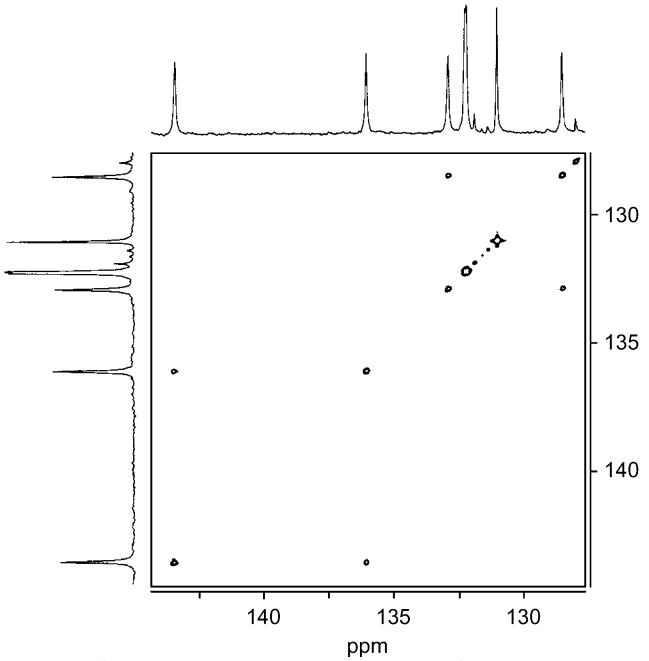
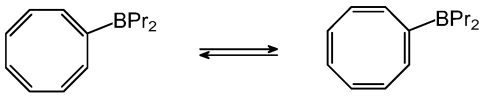


Fig. 2 2D ^{13}C EXSY spectrum (200 MHz, 25 °C, [^{2}H$_8$]toluene), matrix size 1024 × 1024, mixing time τ_m 0.25 s. Intensive cross-peaks C^2↔C^8 and C^3↔C^7 indicate the bond shifting to be the mechanism of fluctionality in **4**. Cross-peak C^4↔C^6 could not be observed in this spectrum due to the closeness of the corresponding signals. However, the existence of such an exchange was confirmed by a ^{1}H NOESY experiment.

Line shape analysis performed for ten ^{13}C spectra of **4** recorded at different temperatures in the temperature interval 0–50 °C allowed us to obtain activation parameters for the bond shifting in **4**:



$\Delta G^{\ddagger}(298) = 67.7 \pm 0.1$ kJ mol^{-1}; $\Delta H^{\ddagger} = 58.1 \pm 0.8$ kJ mol^{-1}; $\Delta S^{\ddagger}$ mol^{-1} K^{-1}

The values of the activation parameters for bond shifting in **4** are very close to those of other monosubstituted cyclooctatetraenes.[8] Therefore, it can be concluded that interaction of the unoccupied 2p-AO of boron atom with the cyclic π-system in **4** does not significantly affect the process of bond shifting.

This work was partly supported by the International Science Foundation (grant no. M3Y000) and by the Russian Foundation for Fundamental Researches (grant no. 94-03-08857).

Table 1 NMR characteristics of cyclooctatetraenyl(dipropyl)borane **4**.[a]

Atom number	δ_H (ppm)	Coupling constants/Hz[b]	δ_C (ppm)
1	–	–	152.4
2	6.50	J(H^2,H^3) 3.5	143.3
3	6.01	J(H^3,H^4) 8.2	132.8
4	5.87	J(H^4,H^5) 3.7	132.2
5	5.78	J(H^5,H^6) 11.7	131.1
6	5.84	J(H^6,H^7) 4.5	132.1
7	5.74	J(H^7,H^8) 11.4	128.7
8	6.18		135.9

[a]Obtained on a Bruker AMX-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C). [b]Obtained from a double-quantum phase sensitive COSY experiment.

References

1 (*a*) R. Wiltstätter and E. Waser, *Dtch. Chem. Ges.*, 1911, **44**, 3423; (*b*) R. Wiltstätter and M. Heidelberger, *Dtch. Chem. Ges.*, 1913, **46**, 517.
2 L. A. Paquette, *Tetrahedron*, 1975, **31**, 2855.
3 L. A. Paquette, *Acc. Chem. Res.*, 1993, **26**, 57.
4 C. B. Gorman, E. J. Ginsburg and R. H. Grubbs, *J. Am. Chem. Soc.*, 1993, **115**, 1397.
5 (*a*) Yu. N. Bubnov, *Pure Appl. Chem.*, 1987, **59**, 895; (*b*) Yu. N. Bubnov, *Pure Appl. Chem.*, 1991, **63**, 361.
6 (*a*) M. E. Gurskii, I. D. Gridnev, A. V. Geiderikh, A. V. Ignatenko, Yu. N. Bubnov, V. I. Mstislavsky and Yu. A. Ustynyuk, *Organometallics*, 1992, **11**, 4056; (*b*) I. D. Gridnev, M. E. Gurskii, A. V. Ignatenko, Yu. N. Bubnov and Yu. V. Il'ichev, *Organometallics*, 1993, **12**, 2487.
7 J. Gasteiger, G. E. Gream, R. Huisgen, W. E. Konz and U. Shegg, *Chem. Ber.*, 1971, **104**, 2412.
8 F. A. L. Anet, A. J. R. Bourn and Y. S. Lin, *J. Am. Chem. Soc.*, 1964, **86**, 3576.
9 R. Laatikainen, *J. Magn. Reson.*, 1985, **64**, 375.

Received: Moscow, 2nd August 1994
Cambridge, 13th September 1994; Com. 4/04834B