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Correlation of Experimentally Obtained Isomer Equilibrium Stability Data with MNDO Calculations for Various Chloro and Methyl Derivatives of *closo*-2,4-$C_2B_5H_7$

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Application of the MNDO semiempirical MO method to isomer sets among substituted *closo*-2,4-$C_2B_5H_7$ compounds is used to predict relative stabilities. Specifically, the MNDO-derived stabilities for the carboranes *B*-CH_3-*closo*-2,4-$C_2B_5H_6$ (three isomers), *B*-Cl-*closo*-2,4-$C_2B_5H_6$ (three isomers), *B,B'*-X_2-*closo*-2,4-$C_2B_5H_5$ (X = CH_3, Cl; five isomers each), and *B*-CH_3-*B'*-Cl-*closo*-2,4-$C_2B_5H_5$ (eight isomers) are correlated with experimental data obtained from thermal rearrangement-equilibration studies. In general, the MNDO order of stabilities, within each isomer set, parallel the experimental observations. Also, there is good concurrence of MNDO-predicted dipole moments with experimental volatilities.

Introduction

Most molecular orbital studies of carboranes have focused on the parent (i.e., unsubstituted) cage compounds.[1-3] The few investigations concerning derivatives of carboranes have largely concentrated on potential cage opening or cage charge distributions.[1x,2a,4,5] In the present study the MNDO semiempirical MO method[3,6] is implemented to examine relative stabilities of a number of *closo*-2,4-$C_2B_5H_7$ derivatives. Ab initio methods with a high-quality basis set would be unsuitable, because of obvious computer time constraints, for the present study. The MNDO program is readily accessible and, as previously noted in the literature, is probably as good as, if not better than, other

Table I. MNDO-Calculated Heats of Formation and Dipole Moments for *B*-CH_3- and *B,B'*-$(CH_3)_2$- Derivatives of *closo*-2,4-$C_2B_5H_7$

compd	MNDO ΔH_f, cal	MNDO $\Delta\Delta H_f$,[a] J	dipole moments, D
	Symmetry Constrained (SC)[b]		
1-CH_3-	18628	3021	1.35
3-CH_3-	17906	0	1.70
5-CH_3-	18900	4157	0.94
1,3-$(CH_3)_2$-	3017	0	1.75
1,5-$(CH_3)_2$-	3935	3841	1.09
1,7-$(CH_3)_2$-	3568	2307	1.23
3,5-$(CH_3)_2$-	3044	137	1.38
5,6-$(CH_3)_2$-	4514	6263	0.61
	Enforced Planar (EP)[b]		
1-CH_3-	18604	2998	1.35
3-CH_3-	17887	0	1.70
5-CH_3-	18900	4235	0.94
1,3-$(CH_3)_2$-	2969	0	1.75
1,5-$(CH_3)_2$-	3911	3941	1.09
1,7-$(CH_3)_2$-	3500	2223	1.22
3,5-$(CH_3)_2$-	3049	337	1.38
5,6-$(CH_3)_2$-	4485	6343	0.61
	Totally Optimized (TO)[b]		
1-CH_3-	18629	2961	1.35
3-CH_3-	17922	0	1.69
5-CH_3-	18909	4092	0.94
1,3-$(CH_3)_2$-	2988	0	1.75
1,5-$(CH_3)_2$-	3928	3931	1.09
1,7-$(CH_3)_2$-	3525	2246	1.19
3,5-$(CH_3)_2$-	3081	387	1.38
5,6-$(CH_3)_2$-	4500	6325	0.61

[a] Values derived from column 2; the isomer with the lowest ΔH_f in column 2, within each isomer set, is arbitrarily assigned $\Delta\Delta H_f$ = 0. [b] Consult text for description of geometrical constraints imposed.

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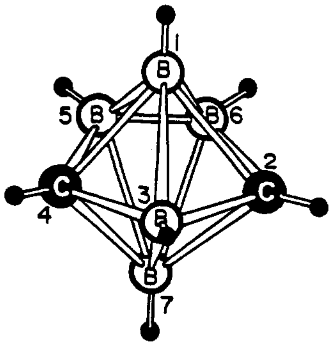

Figure 1. Ball and stick model and cage numbering of the parent *closo*-2,4-$C_2B_5H_7$.

semiempirical methods for heats of formation computations.[3b,7,8] Fortunately, a local minimum on the MNDO potential energy surface is realized[3b] for the experimentally verified framework[9-12] of the parent *closo*-2,4-$C_2B_5H_7$.

Specifically, we set out to determine how well MNDO can predict the relative stabilities of *B*-monomethyl-,[13-15] *B*-monochloro-,[15-17] *B,B'*-dimethyl-,[15,18] *B,B'*-dichloro-,[16,17] and *B*-methyl-*B'*-chloro-*closo*-2,4-dicarbaheptaborane[15] isomers. For comparison purposes, experimentally derived stability data for those compounds within each of the five isomer sets are available from thermal (variously, from 295 to 340 °C) equilibration results.

Experimental Section

Calculations were performed by employing a previously described standard MNDO procedure,[6a] Version QCPE379, modified by us for the CSULA CDC-170 computer. Three different levels of input geometry constraints were applied in attempts to optimize the total molecular energy and heats of formation of each of the pentagonal-bipyramidal *closo*-2,4-$C_2B_5H_7$ derivatives: (a) symmetry constrained (SC); (b) enforced planarity (EP) upon the equatorial C_2B_3 pentagon; (c) total optimization (TO) of the equilibrium geometry. In the symmetry-constrained approach (a), symmetry elements were imposed on those bond lengths, bond angles, and dihedral angles that are considered to be equivalent as a result of obvious overall molecular symmetry (see Figure 1). For the EP approach (b) the equatorial C_2B_3 pentagon was held planar while all other parameters were optimized. And in approach c the calculations were carried out, of course, with no imposed symmetry or other restrictions.

The initial input geometry of the parent carborane, *closo*-2,4-$C_2B_5H_7$, was based upon that determined by microwave spectroscopy.[9,10] For the purposes of MNDO calculations on the chloro and methyl derivatives, the appropriate geometry input data for *closo*-2,4-$C_2B_5H_7$ were constructed by replacing the appropriate hydrogens bonded to boron, in the parent compound, by either chlorine or carbon atoms directed along the former B–H bond vectors; these were initially set at distances of 1.823[19] and 1.491 Å,[20] respectively. Atom labeling and the structure of the parent *closo*-2,4-$C_2B_5H_7$ and derivatives are illustrated in Figure 1.

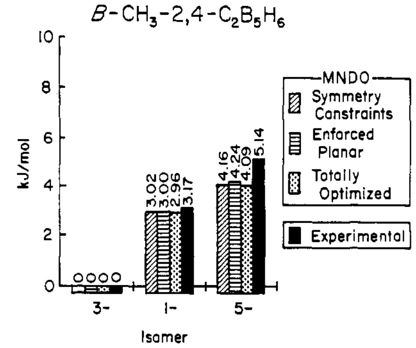

Figure 2. Bar graph comparison of the relative MNDO derived enthalpies (column 3, Table I) with experimental values[14,15] for the three *B*-methyl derivative isomers of *closo*-2,4-$C_2B_5H_7$. The isomer with the lowest enthalpy in the set is arbitrarily assigned a base value $\Delta\Delta H = 0$.

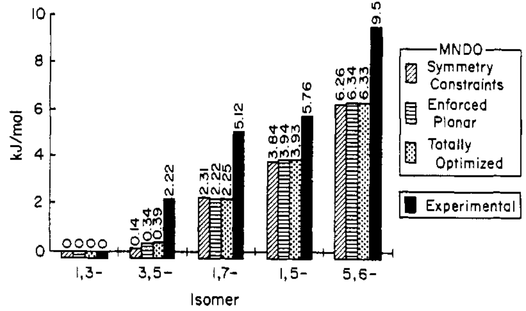

Figure 3. Bar graph comparison of the relative MNDO derived enthalpies (column 3, Table I) with experimental values[15,18] for the five *B,B'*-dimethyl derivative isomers of *closo*-2,4-$C_2B_5H_7$. The isomer with the lowest enthalpy in the set is arbitrarily assigned a base value $\Delta\Delta H = 0$.

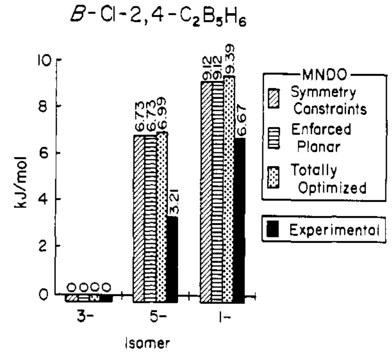

Figure 4. Bar graph comparison of the relative MNDO derived enthalpies (column 3, Table II) with experimental values[15] for the three *B*-chloro derivative isomers of *closo*-2,4-$C_2B_5H_7$. The isomer with the lowest enthalpy in the set is arbitrarily assigned a base value $\Delta\Delta H = 0$.

In two cases the input geometry, as estimated in this fashion, was unsatisfactory for locating a closo-cage (TO) MNDO derived energy minimum; in those instances this procedure resulted in a classical norbornane type of structure, as experienced by us upon application of the TO approach to the 1-CH_3-3-Cl- and 1,3-Cl_2- derivatives. Additional methods were then implemented in order to obtain an (TO) MNDO optimized closo-cage structure. For the 1-CH_3-3-Cl- isomer the MNDO optimized 1-CH_3-*closo*-2,4-$C_2B_5H_6$ geometry was appropriately edited to provide a 1-CH_3-3-Cl- input geometry. This structure satisfactorily (TO) MNDO optimized to a 1-CH_3-3-Cl-*closo*-2,4-$C_2B_5H_5$ cage structure. A TO closo cage structure for the 1,3-Cl_2- derivative could not be obtained from the above procedures. This problem was solved by inputing (SC) MNDO 1,3-Cl_2- output for a (TO) MNDO calculation; consequently, an energy minimum for a 1,3-Cl_2-*closo*-2,4-$C_2B_5H_5$ framework was realized. It is important to note that a local closo-cage energy minimum was found on the (TO) MNDO potential energy surface for each of the compounds studied.

Both the input and output geometries for each isomer were verified by using PROPHET (Bolt, Beranek and Newman, Inc.) and programs

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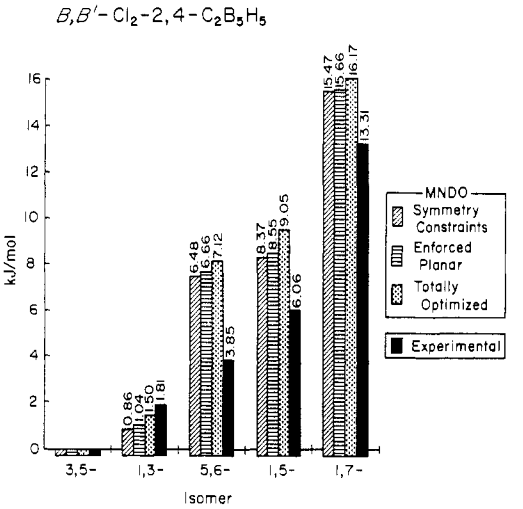

Figure 5. Bar graph comparison of the relative MNDO derived enthalpies (column 3, Table II) with experimental values[17] for the five *B*-dichloro derivative isomers of *closo*-2,4-$C_2B_5H_7$. The isomer with the lowest enthalpy in the set is arbitrarily assigned a base value $\Delta\Delta H = 0$.

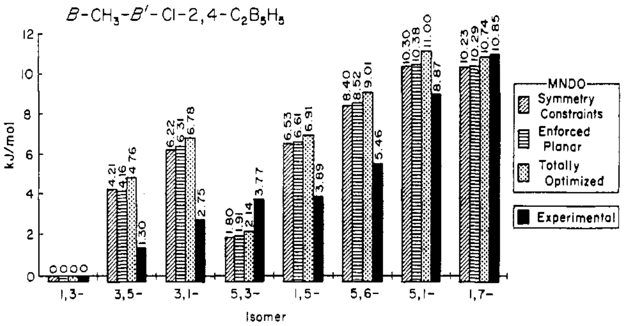

Figure 6. Bar graph comparison of the relative MNDO derived enthalpies (column 3, Table III) with experimental values[15] for the eight *B*-methyl-*B'*-chloro derivative isomers of *closo*-2,4-$C_2B_5H_7$. The isomer with the lowest enthalpy in the set is arbitrarily assigned a base value $\Delta\Delta H = 0$.

CRYST, MAST, MOLDAT, and EDITMODEL available through the National Institutes of Health.

Results and Discussion

The MNDO calculated heats of formation for various *B*-methyl- and *B*-chloro-substituted *closo*-2,4-$C_2B_5H_7$ isomers are given in Tables I–III. Representative MNDO derived (relative) enthalpies, column 3 of the tables, are compared to those experimentally derived[14,15,17] in Figures 2–6. The comparisons are striking. When it is noticed that the differences in experimental $\Delta\Delta H_f$ values between the most and least stable isomers within a family of compounds are less than 17 kJ (4+ kcal), it is somewhat astonishing that the semiempirical MNDO MO approach can accurately predict isomer stability orders (with only a minor deviation noticed in the *B*-CH_3-*B'*-Cl-*closo*-2,4-$C_2B_5H_5$ system) and also give a reasonable estimate of the energy differences in these nonclassical systems. This favorable comparison may well be attributed, in large part, to the close structural similarity, and bond type, between members of each isomer family.

Specifically, both the MNDO and experimental results show the following isomer stability order among the mono- and disubstituted *closo*-$C_2B_5H_7$ compounds *B*-X-*closo*-2,4-$C_2B_5H_6$ (three isomers for each X) and *B,B'*-X_2-*closo*-2,4-$C_2B_5H_5$ (X = CH_3, Cl; five isomers each):

B-monochloro: 3- > 5- > 1-

B-monomethyl: 3- > 1- > 5-

B,B'-dichloro: 3,5- > 1,3- > 5,6- > 1,5- > 1,7-

B,B'-dimethyl: 1,3- > 3,5- > 1,7- > 1,5- > 5,6-

Table II. MNDO-Calculated Heats of Formation and Dipole Moments for *B*-Cl- and *B,B'*-Cl_2- Derivatives of *closo*-2,4-$C_2B_5H_7$

compd	MNDO ΔH_f, cal	MNDO $\Delta\Delta H_f$,[a] J	dipole moments, D
	Symmetry Constrained (SC)[b]		
1-Cl-	10711	9123	1.70
3-Cl-	8530	0	0.15
5-Cl-	10138	6727	2.44
1,3-Cl_2-	−14388	857	1.21
1,5-Cl_2-	−12592	8371	2.56
1,7-Cl_2-	−10895	15471	1.00
3,5-Cl_2-	−14593	0	1.25
5,6-Cl_2-	−13045	6476	3.18
	Enforced Planar (EP)[b]		
1-Cl-	10711	9122	1.70
3-Cl-	8531	0	0.15
5-Cl-	10138	6726	2.44
1,3-Cl_2-	−14387	1043	1.21
1,5-Cl_2-	−12592	8551	2.56
1,7-Cl_2-	−10894	15656	1.00
3,5-Cl_2-	−14636	0	1.24
5,6-Cl_2-	−13045	6655	3.18
	Totally Optimized (TO)[b]		
1-Cl-	10734	9390	1.69
3-Cl-	8490	0	0.17
5-Cl-	10159	6985	2.44
1,3-Cl-	−14388	1499	1.21
1,5-Cl_2-	−12584	9048	2.55
1,7-Cl_2-	−10882	16170	0.99
3,5-Cl_2-	−14747	0	1.20
5,6-Cl_2-	−13046	7116	3.17

[a] Values derived from column 2; the isomer with the lowest ΔH_f in column 2, within each isomer set, is arbitrarily assigned $\Delta\Delta H_f = 0$. [b] Consult text for description of geometrical constraints imposed.

Table III. MNDO-Calculated Heats of Formation and Dipole Moments for *B*-CH_3-*B'*-Cl- Derivatives of *closo*-2,4-$C_2B_5H_7$

compd	MNDO ΔH_f, cal	MDNO $\Delta\Delta H_f$,[a] J	dipole moments, D
	Symmetry Constrained (SC)[b]		
1-CH_3-3-Cl-	−6791	0	0.65
1-CH_3-5-Cl-	−5230	6530	2.56
1-CH_3-7-Cl-	−4345	10232	2.19
3-CH_3-1-Cl-	−5305	6217	2.07
3-CH_3-5-Cl-	−5786	4205	2.93
5-CH_3-1-Cl-	−4330	10296	1.56
5-CH_3-3-Cl-	−6360	1802	0.63
5-CH_3-6-Cl-	−4782	8404	2.27
	Enforced Planar (EP)[b]		
1-CH_3-3-Cl-	−6832	0	0.67
1-CH_3-5-Cl-	−5252	6608	2.55
1-CH_3-7-Cl-	−4374	10285	2.20
3-CH_3-1-Cl-	−5324	6309	2.07
3-CH_3-5-Cl-	−5839	4155	2.93
5-CH_3-1-Cl-	−4352	10375	1.57
5-CH_3-3-Cl-	−6375	1911	0.63
5-CH_3-6-Cl-	−4796	8518	2.27
	Totally Optimized (TO)[b]		
1-CH_3-3-Cl-	−6940	0	0.74
1-CH_3-5-Cl-	−5288	6908	2.56
1-CH_3-7-Cl-	−4372	10744	2.22
3-CH_3-1-Cl-	−5320	6777	2.07
3-CH_3-5-Cl-	−5802	4759	2.94
5-CH_3-1-Cl-	−4310	11001	1.55
5-CH_3-3-Cl-	−6427	2144	0.65
5-CH_3-6-Cl-	−4787	9008	2.26

[a] Values derived from column 2; the isomer with the lowest ΔH_f in column 2, within each isomer set, is arbitrarily assigned $\Delta\Delta H_f = 0$. [b] Consult text for description of geometrical constraints imposed.

Of the eight *B*-methyl-*B'*-chloro-substituted isomers of *closo*-2,4-$C_2B_5H_7$,[15] MNDO (all approaches, see procedures) very nearly predicts the correct stability order:

experimental (CH_3,Cl): 1,3- > 3,5- > 3,1- > 5,3- > 1,5- > 5,6- > 5,1- ≥ 1,7-

MNDO (CH_3,Cl): 1,3- > 5,3- > 3,5- >3,1- > 1,5- > 5,6- > 1,7- ≥ 5,1-

Only the 5-CH_3-3-Cl- isomer is "out of order". This and other smaller differences in $\Delta\Delta H$ magnitude between MNDO and experimental results may be attributed to anyone of a number of factors: (a) The experimental enthalpy results depend on the assumption that entropy differences between isomers are due to symmetry changes alone in the utilization of the relationship

$$\Delta H = -RT \ln K + T\Delta(R \ln W)$$

(where W is the number of distinguishable configurations[21] that a compound may assume[14,15,17,18]) for calculating experimental ΔH differences between isomers. This may be a very good first-order approximation but may not be rigorous. (b) Reasonable errors encountered in the experimentally obtained isomer equilibrium values may also account for some of the differences. (c) Problems inherent in the use of a semiempirical MO approach (MNDO in this instance) may account for the small inconsistencies.

This study may well represent the first occasion that isomer stabilities with such small energy differences are reliably predicted by any MO method. And this is all the more remarkable upon noticing that MNDO calculated energies for the *closo*-dicarbaheptaborane structures appear to be local energy minima; a norbornane (bicyclo[2.2.1]heptane) framework with carbons at the bridgehead appears to be considerably more stable (by about 40–80 kJ) than the isomeric pentagonal-bipyramidal skeletal atom arrangement for all derivatives in this study.

Dipole Moments

The *closo*-2,4-$C_2B_5H_7$ dipole moment[10] is expected, on the basis of earlier dipole moment work on *closo*-$C_2B_{10}H_{12}$ carboranes,[22,23] to be directed along the axis passing through B(3) and bisecting the B(5,6) bond;[10] the carbons are at the positive end of the cage dipole with the negative end of the dipole in the direction of the B(5,6) bond. The MNDO calculated dipole moment of the parent *closo*-2,4-$C_2B_5H_7$, 1.24 D,[3b] is reasonably close to the experimentally obtained value, 1.32 D,[10] determined by microwave/Stark effect techniques. In the present study MNDO calculated dipole moments (Tables I–III, column 4) for all of the B- (mono- and di-) substituted compounds containing Cl- and CH_3-attached groups predict the following volatility trends among *closo*-2,4-$C_2B_5H_7$ derivatives:

5-CH_3- > 1-CH_3- > 3-CH_3-

3-Cl- > 1-Cl- > 5-Cl-

5,6-$(CH_3)_2$- > 1,5-$(CH_3)_2$- > 1,7-$(CH_3)_2$- > 3,5-$(CH_3)_2$- > 1,3-$(CH_3)_2$-

1,7-Cl_2- > 1,3-Cl_2- > 3,5-Cl_2- > 1,5-Cl_2- > 5,6-Cl_2-

5-CH_3-3-Cl- > 1-CH_3-3-Cl- > 5-CH_3-1-Cl- > 3-CH_3-1-Cl- > 1-CH_3-7-Cl- > 5-CH_3-6-Cl- >1-CH_3-5-Cl- > 3-CH_3-5-Cl-

In those instances where the experimental volatility trends are known, *B*-CH_3-,[14] *B*-Cl-,[16] and *B*,*B'*-Cl_2-,[17] there is qualitative agreement with those trends predicted by MNDO-derived dipoles in each group. The only exception to the favorable comparison of these trends appears to be a reversal of the 1,7-Cl_2- and 1,3-Cl_2- isomers (i.e. the 1,3-Cl_2- isomer appears to be more volatile than the 1,7-Cl_2- isomer[17]).

Estimates of group dipoles (i.e. *B*-Cl, *B*-CH_3) can be made by vector dipole analyses of the mono-B-substituted compounds, and the assumption that the pentagonal-bipyramidal cage contribution is 1.24 D (see above). Values of 1.2–1.4 D for *B*-Cl and 0.45–0.55 D for *B*-CH_3 are derived in this fashion.

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Registry No. 1-CH_3-*closo*-2,4-$C_2B_5H_6$, 23810-31-3; 3-CH_3-*closo*-2,4-$C_2B_5H_6$, 23940-13-8; 5-CH_3-*closo*-2,4-$C_2B_5H_6$, 23810-32-4; 1,3-$(CH_3)_2$-*closo*-2,4-$C_2B_5H_5$, 68297-89-2; 1,5-$(CH_3)_2$-*closo*-2,4-$C_2B_5H_5$, 68238-17-5; 1,7-$(CH_3)_2$-*closo*-2,4-$C_2B_5H_5$, 23753-78-8; 3,5-$(CH_3)_2$-*closo*-2,4-$C_2B_5H_5$, 68238-16-4; 5,6-$(CH_3)_2$-*closo*-2,4-$C_2B_5H_5$, 58548-76-8; 1-Cl-*closo*-2,4-$C_2B_5H_6$, 28347-69-5; 3-Cl-*closo*-2,4-$C_2B_5H_6$, 28347-93-5; 5-Cl-*closo*-2,4-$C_2B_5H_6$, 28347-92-4; 1,3-Cl_2-*closo*-2,4-$C_2B_5H_5$, 71849-89-3; 1,5-Cl_2-*closo*-2,4-$C_2B_5H_5$, 71849-88-2; 1,7-Cl_2-*closo*-2,4-$C_2B_5H_5$, 71849-91-7; 3,5-Cl_2-*closo*-2,4-$C_2B_5H_5$, 71849-90-6; 5,6-Cl_2-*closo*-2,4-$C_2B_5H_5$, 71849-86-0; 1-CH_3-3-Cl-*closo*-2,4-$C_2B_5H_5$, 102614-52-8; 1-CH_3-5-Cl-*closo*-2,4-$C_2B_5H_5$, 79568-29-9; 1-CH_3-7-Cl-*closo*-2,4-$C_2B_5H_5$, 102630-01-3; 3-CH_3-1-Cl-*closo*-2,4-$C_2B_5H_5$, 102614-51-7; 3-CH_3-5-Cl-*closo*-2,4-$C_2B_5H_5$, 102648-58-8; 5-CH_3-1-Cl-*closo*-2,4-$C_2B_5H_5$, 102614-50-6; 5-CH_3-3-Cl-*closo*-2,4-$C_2B_5H_5$, 102630-00-2; 5-CH_3-6-Cl-*closo*-2,4-$C_2B_5H_5$, 79550-11-1.

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