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Enthalpies of Formation and Bond Energies in Lithium, Beryllium, and Boron Derivatives. A Theoretical Attempt for Data Rationalization

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For a set of small XYH_n molecules (where X stands for Li, Be, or B and Y is one of the second-row atoms), we have calculated the enthalpies of formation at the MP4 = SDTQ/6-311++G(3df,2p) level of theory by using MP2 = FULL/6-31 G(d,p) fully optimized structures. The obtained values are expected to be in the range of the so-called "chemical accuracy" (±1 kcal/mol). Some alkyl derivatives of the previous XYH_n compounds have been studied at the RHF/6-31G* level (with fully optimized geometries). The theoretical enthalpies of formation reproduce most of the available experimental results in a quite satisfactory manner. All the collected (experimental or theoretical) data are used to build a bond-energy table, which includes lithium, beryllium, and boron atoms.

Introduction

The study of lithium, beryllium, and boron compounds is a challenge both from theoretical and experimental points of view. Experimental difficulties arise from the transient, explosive, or toxic character of those electronically deficient molecules. Nevertheless, thermochemical data are available[2-5] for some derivatives, especially for medium-size alkyl-, alkoxy-, hydroxy-, and fluoroboranes, fluoro- and hydroxyberyllium hydrides, and methyl- and hydroxylithium. Missing data make systematic analyses difficult. From the theoretical point of view, the accuracy of the thermochemical estimates depends strongly on the level of theory. Recent developments in computer and computing sciences now give access to accurate electronic energies as long as appropriate methodologies are chosen. First of all, one needs large basis sets (minimum-type basis sets may give wrong stationary points at the Hartree–Fock level[6]). Moreover, the electron correlation is also of major importance for the smallest derivatives.

Experimental data concerning these compounds are lacking; efforts have been made for a few years to estimate as accurately as possible the missing values. The number of papers on this subject increase in an exponential manner. Many significant theoretical contributions in this field are quite recent.[7-14] They show that theoretical methods may be of great interest.

In this study, we try to give thermochemical information about molecules that involve at least one lithium, beryllium, or boron atom and one other heavy atom from the second row of Mendeleev's table. We also study the alkyl derivatives of the previous molecules. Our purpose is to obtain a set of consistent and accurate standard enthalpies of formation at room temperature for gas-phase species (ΔH_f) and to build a bond-energy (E_b) table.

Theoretical Enthalpies of Formation of XYH_n Compounds

Let us first consider molecules containing only two heavy atoms. In this case, the obtainment of accurate results requires a large but feasible theoretical effort. Papers[15-17] published in the last decade show that the usual split valence polarized basis sets have to be increased by additional d, f, and diffuse (+) functions. Then, the Møller–Plesset perturbation theory limited to the fourth order of development (MP4) allows us to predict enthalpies of formation in a satisfactory manner. In this study, the calculations have been performed at the MP4 level (including single, double, triple, and quadruple replacements) by using the 6-311++G(3df,2p) basis set. There are single-point calculations on MP2/6-31 G(d,p) fully optimized structures reported in previous works.[6,18] To calculate the enthalpies of formation, one takes advantage of the hydrogenation reaction. This reaction is less sensitive to the fourth-order error of truncation of the perturbation than other reactions[19] such as the isogyric[20] ones.[21] The fol-

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Table I. Electronic Energies (au) at the MP4 Level and Standard Enthalpies of Formation at 298.15 K (kcal/mol)

$XYN_n{}^m$		6-311++G(3df,2p) level			6-31+G(2df,p) level			exptl level
		E(MP4)^a	ΔH_f isogyric exact	ΔH_f hydrog. exact	ΔH_f isogyric combined	ΔH_f isogyric exact	ΔH_f hydrog. exact	ΔH_f
LiH	$^1\Sigma^+$	-8.020 07	33.43^b		35.36^c	$35.39^{b,c}$		33.61 ± 0.01^d
LiBeH	$^1\Sigma^+$	-22.691 61	75.59	75.77	73.63^c	73.55^c	73.34^e	
$LiBH_2$	$^1A_1$	-33.361 47	67.73	67.91	65.64^c	66.49^c	66.91^e	
$LiCH_3$	$^1A_1$	-47.263 04	25.00	25.23	22.52^c	24.17^c	24.00^3	15.22^f
$LiNH_2$	$^1A^1$	-63.339 43	10.18	8.41	4.71^c	9.93^c	7.50^e	
LiOH	$^1\Sigma^+$	-83.234 64	-57.77	-57.35	-62.09^c	-56.61^c	-57.50^e	-56 ± 1.5^d
BeH_2	$^1\Sigma g^+$	-15.844 10	39.31^b		37.82^c	$37.75^{b,c}$		$[30]^d$
HBeBeH	$^1\Sigma g^+$	-30.503 03	88.44	88.44	85.51^c	87.08^c	90.65^e	
$HBeBH_2$	$^1A_1$	-41.187 53	71.85	71.85	68.20^c	69.60^c	73.67^e	
$HBeCH_3$	$^1A_1$	-55.102 03	21.24	21.29	14.49^c	15.47^c	22.83^e	
$HBeNH_2$	$^1A_1$	-71.182 58	3.74	1.79	-1.61^c	3.42^c	3.16^e	
HBeOH	$^1A'$	-91.069 15	-59.57	-59.34	-61.26^c	-57.89^c	-57.25^e	
HBeF	$^1\Sigma^+$	-115.096 38	-79.98	-78.97	-82.61^c	-78.05^c	-77.09^e	-76.72 ± 6.7^d
BH_3	$^1A'$	-26.532 78	21.94^b		$20.16^{g,h}$	19.76^{b-h}		22^j
H_2BBH_2	^1E	-51.889 81	45.36	45.35	41.84^i	42.73^k	47.12^k	
HBH_2BH	$^1A_1$	-51.892 76	43.90	43.90	42.61^g	41.87^k	46.26^k	
BH_2CH_3	$^1A'$	-65.789 12	4.95	5.00	1.37^i	1.69^k	6.55^k	
BH_2NH_2	$^1A_1$	-81.885 00	-21.06	-23.02	-26.61^i	-23.51^k	-21.96^k	
BH_2OH	$^1A'$	-101.746 36	-68.96	-68.73	-71.67^i	-70.47^k	-67.40^k	-69.4^l
BH_2F	$^1A_1$	-125.752 62	-77.60	-76.59	80.06^i	-78.26^k	-75.10^k	

[a] Some reference energies are also available from ref 19. [b] Reference 19. [c] Reference 18. [d] Reference 3. [e] Calculated from data of ref 18. [f] Reference 2. [g] Reference 6. [h] Reference 22. [i] Reference 34. [j] Reference 29. [k] Unpublished results. [l] Reference 5. [m] Reaction used electronic energy.

lowing relations give access to the enthalpies of formation (ΔH_f):

$$H_{n'}XYH_{n''} + H_2 \rightarrow XH_{n'+1} + YH_{n''+1}$$

$$\Delta H_f(XYH_{n'+n''}) = \Delta H_f(XH_{n'+1}) + \Delta H_f(YH_{n''+1}) - \Delta H_r \qquad (1)$$

where ΔH_r is the heat of hydrogenation at 298.15 K obtained from theoretical reaction energies for fixed nuclei corrected for ZPE and temperature with data from ref 6, 18, and 19.

We obtain the values listed in Table I. This table also contains some comparisons with other theoretical or experimental results. From the theoretical point of view, the larger the basis set, the more independent are the theoretical enthalpies of formation of the reaction. The use of combined energies instead of exact values (according to the procedure proposed by Pople et al.[15]) leads to underestimated enthalpies of formation.[18,23] Comparison between the theoretical and experimental values contains only a very few terms. Nevertheless, for well-established values, coincidence has been achieved except for methyllithium. In this case, the experimental enthalpy of formation is 10 kcal/mol lower than our theoretical result. Such a large discrepancy has already been pointed out elsewhere,[18,24] and the measurement of the heat of sublimation (into monomer) still remains questionable. From the theoretical CH_3Li BDE (bond dissociation energy) reported by Ahlrichs et al.,[25] one obtains a ΔH_f of 26.7 kcal/mol. In a recent work, Schleyer et al. use 26.9 kcal/mol for the methyllithium enthalpy of formation.[26] All these values are in agreement with our results (see Table I). For borane(3), the MP4/6-311++G(3df,2p) enthalpy of formation compares well with the theoretical results of Pople et al.[21] and Martin et al.[27] They are lower than the ones currently reported in thermochemical tables (JANAF[3] gives 25.5 ± 2.4 kcal/mol and NBS[28] reports 23.9 kcal/mol). Nevertheless, a recent experimental result obtained by Ruscic et al.[29] coincides with the values given in Table I. Let us note that this enthalpy of formation, combined with the best binding energy of B_2H_6,[30] suggests that diborane(6) has an enthalpy of formation close to 4.4 kcal/mol (which is 4 kcal/mol lower than the JANAF[3] recommended value). Diborane(4) has been known for a long time to have two structures,[31] one with a double bridge and another with a B–B central single bond. We found that the former is 1.5 kcal/mol more stable than the latter. Procedures that use a combination of the energies (beyond the 6-31[1]G** level) give only a difference of 0.1 kcal/mol, also in favor of the bridged structure.[32-34] Finally, let us mention that for BeH_2, which is experimentally unknown, the theoretical value of Pople et al. (39.5 kcal/mol[15]) and the recent result of Martin et al. (40.6 kcal/mol[27]) are in agreement with our result (39.3 kcal/mol).

Enthalpies of Formation of the Alkyl Derivatives

We now consider molecules that can be obtained from those given in Table I if we exchange one or more hydrogen atom(s) for an alkyl group(s). Such molecules become too large, and the previous procedure for obtaining the enthalpies of formation becomes too expansive. When only calculations at the Hartree–Fock level are feasible, one uses model chemical reactions in which the total correlation energy and the error of the basis set truncation are ap-

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Table II. Total Energies (au) at the HF/6-31G* Level and Selected Enthalpies of Formation (kcal/mol) for the Reference Compounds

compds	ΔH_f	ref	E(6-31G*)
BeH_2 ($^1\Sigma g^+$)	39.31	19	−15.765 93
BH_3 ($^1A_1'$)	21.94	19	−26.390 01
CH_4 ($^1T_2$)	−17.78	4	−40.195 17
NH_3 ($^1A_1$)	−10.97 ± 0.1	3	−56.184 36
OH_2 ($^1A_1$)	−57.8 ± 0.01	3	−76.010 75
HBeLi ($^1\Sigma^+$)	75.77	*a*	−22.609 27
BH_2Li ($^1A_1$)	67.91	*a*	−33.209 94
CH_3Li ($^1A_1$)	25.23	*a*	−47.015 54
NH_2Li ($^1A_1$)	8.41	*a*	−63.041 96
LiOH ($^1\Sigma^+$)	−56 ± 1.5	3	−82.903 29
HBeBeH ($^1\Sigma g^+$)	88.44	*a*	−30.378 82
$HBeBH_2$ ($^1A_1$)	71.85	*a*	−40.997 68
$HBeCH_3$ ($^1A_1$)	21.29	*a*	−54.816 01
$HBeNH_2$ ($^1A_1$)	1.79	*a*	−70.849 87
HBeOH ($^1A'$)	−59.34	*a*	−90.705 21
HBeF ($^1\Sigma^+$)	−78.97	*a*	−114.727 16
BH_2BH_2 (^1E)	45.35	*a*	−51.634 70
BH_2CH_3 ($^1A'$)	5.00	*a*	−65.441 42
BH_2NH_2 ($^1A_1$)	−23.02	*a*	−81.489 10
BH_2OH ($^1A'$)	−69.40	5	−101.321 40
BH_2F ($^1A_1$)	−76.59	*a*	−125.322 13
OLi_2 ($^1\Sigma g^+$)	−39.9 ± 0.36	3	−89.769 90
BeF_2	−190.25	3	−213.677 77
$Be(OH)_2$	−156.4	38	−165.635 91
BF_2BF_2	−344	37	−447.366 92
$B(CH_3)_3$	−29.3	2	−143.542 26
$BH(OH)_2$	−153.1	5	−176.253 37
$B(OH)_3$	−237	5	−251.181 72
$BH(OCH_3)_2$	−138.4	5	−254.299 65
$B(OCH_3)_3$	−214.6	5	−368.249 06
BHF_2	−176.6	5	−224.262 40
BF_3	−271.41	5	−323.195 48
BF_2OH	−260.7	5	−299.192 05
CH_3BF_2	−199	37	−263.317 05
CH_3CH_3	−20.08	4	−79.228 75
$CH_3CH_2CH_3$	−25.02	4	−118.263 65
$(CH_3)_3CH$	−32.07	4	−157.298 96
CH_3NH_2	−5.5	4	−95.209 83
$NH(CH_3)_2$	−4.43	4	−134.238 85
$N(CH_3)_3$	−5.66	4	−173.269 30
CH_3OH	−48.18	4	−115.035 42
CH_3CH_2OH	−56.24	4	−154.075 74
CH_3OCH_3	−43.99	4	−154.064 74

[a] This work, see Table I.

proximately equal in both sides of the equation. It is usually assumed that the necessary condition is the conservation of the type and number of bonds. Isodesmic reactions meet this requirement.[35] Moreover, if the same bonds appear in both sides of the equation, the heat of reaction must be small and vary very little with temperature.[36] Then, for larger molecules than those given in Table I, we use the isodesmic approach. The total energies have been obtained at the HF/6-31G(d) level, using fully optimized structures. Table II contains the electronic energies and the enthalpies of formation of some reference compounds. First, we employ these data to write isodesmic reactions that are able to assure the consistency of theoretical and experimental values (see Table III) This gives indirect comparisons for CH_3BH_2, H_2BBH_2, BH_2F, and HBeOH (they complete the few direct comparisons reported in Table I). The results from Table III are in satisfactory agreement with experimental values. The theoretical predictions reported there seem to be better than other results obtained from earlier treatments, especially MNDO[39,40] or AM1.[41] Taking into account the quality of the theoretical method we are using and the difficulty of obtaining reliable experimental gas-phase values, we believe that the values listed in Table II are not questionable. We think that the largest deviation from the "exact" values does not exceed 1 or 2 kcal/mol.

Let us now generalize the isodesmic approach to a larger set of lithium, beryllium, and boron alkyl derivatives. The HF/6-31G(d) energies, the isodesmic reactions, and the predicted enthalpies of formation are listed in Table IV. Corresponding experimental heats of formation are not available. Nevertheless, we can observe regularities in the thermochemical results. So in the $BH_{3-n}X_n$ series, one finds good correlations between ΔH_f and the number "n" of substituents (n varying from 1 to 3):

for X = CH_3,

$$\Delta H_f = 22.04 - 17.15n$$

for X = OH,

$$\Delta H_f = 14.43 - 83.80n$$

for X = OCH_3,

$$\Delta H_f = 14.30 - 76.31n$$

for X = F,

$$\Delta H_f = 19.96 - 97.41n \qquad (2)$$

The correlation coefficients (ρ) are always larger than 0.9999, and the independent term in the first regression (22 kcal/mol) is nothing but the value of the borane(3) enthalpy of formation. In the beryllium series, one observes also a good linear dependence of ΔH_f with respect to the number of methyl substituents (with n varying from 0 to 2):

for X = CH_3,

$$\Delta H_f = 39.24 - 17.81n \qquad (\rho = 0.9999) \qquad (3)$$

where the independent term corresponds to the BeH_2 enthalpy of formation (39.3 kcal/mol). We can also compare the heats of formation of the methyl and the ethyl derivatives:

$$\Delta H_f(CH_3CH_2X) = 1.08\Delta H_f(CH_3X) - 4.11 \text{ kcal/mol} \qquad (\rho = 0.9996) \quad (4)$$

if X stands for Li, BeH, BH_2, CH_3, NH_2, OH, or F. All these correlations do not establish the accuracy of the enthalpies of formation, but they show the consistency of the values reported in Tables I–IV.

Bond Energies in Alkylboranes

Let us now use a simple thermochemical model in order to widen the comparison to a larger set of experimentally known compounds. The heats of atomization may be split in a sum of bond energies (E_b):

$$\Delta H_a = \sum_b E_b + \text{SE} \qquad (5)$$

The last term in relation 5, namely, the stabilization energy (SE), measures the deviation with respect to the additive scheme.[42] It vanishes when the molecule does not exhibit any special effect. According to a procedure detailed in

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Table III. Comparisons between Theoretical and Experimental Enthalpies of Formation Based on the Selected Values from Table II (kcal/mol)

isodesmic reaction (A + ... → ...)	ΔE_r	ΔH_f(A)	remarks and other values	
$3CH_3BH_2 \rightarrow B(CH_3)_3 + 2BH_3$	1.24	4.5		5.0[a]
$BH_2OH + B(OH)_3 \rightarrow 2BH(OH)_2$	-2.28	-66.9		-68.7[a]
				-69.4[b]
$BH(OCH_3)_2 + 2CH_3OH \rightarrow BH(OH)_2 + 2O(CH_3)_2$	-7.76	-137.0		-138.4[b]
$BH_2F + BF_3 \rightarrow 2BHF_2$	-4.51	-77.3	with $\Delta H_f(BHF_2)$ from *a*	-76.6[a]
		-74.9	with $\Delta H_f(BHF_2)$ from *b*	
$BH_2F + BF_2OH \rightarrow BF_3 + BH_2OH$	-1.69	-77.8	with $\Delta Hf(BH_2OH)$ from *a*	-76.6[a]
		-78.4	with $\Delta H_f(BH_2OH)$ from *b*	
$H_2BBH_2 + 2BHF_2 \rightarrow F_2BBF_2 + 2BH_3$	8.37	44.7		45.4[a]
$2BeHF \rightarrow BeH_2 + BeF_2$	6.66	-78.8		-79.0[a]
$2LiOH \rightarrow OLi_2 + H_2O$	16.27	-57.0		-57.4[a]
				-56[c]
$2HBeOH \rightarrow BeH_2 + Be(OH)_2$	5.72	-61.4	with $\Delta H_f(Be(OH)_2)$ from *d*	-59.3[a]
		-64.1	with $\Delta H_f(Be(OH)_2)$ from *c*	

[a] This work, see Table I. [b] Reference 5. [c] Reference 3. [d] Reference 38.

Table IV. Total Energies (au), Isodesmic Reactions, and Enthalpies of Formation (kcal/mol)

compound	E(6-31G*)	isodesmic reaction	ΔE_r	ΔH_f
$BH(CH_3)_2$	-104.492 31	$2BH(CH_3)_2 \rightarrow BH_2CH_3 + B(CH_3)_3$	0.59	-12.45
$BH_2CH_2CH_3$	-104.473 45	$BH_2CH_2CH_3 + CH_3CH_3 \rightarrow CH_3BH_2 + CH_3CH_2CH_3$	-1.80	1.85
$BH_2CH(CH_3)_2$	-143.505 03	$BH_2CH(CH_3)_2 + CH_3CH_3 \rightarrow BH_2CH_2CH_3 + CH_3CH_2CH_3$	-2.08	-1.00
$BH_2C(CH_3)_3$	-182.537 82	$BH_2C(CH_3)_3 + BH_2CH_2CH_3 \rightarrow 2BH_2CH(CH_3)_2$	0.76	-4.62
$(CH_3)_2BC(CH_3)_3$	-260.634 40	$(CH_3)_2BC(CH_3)_3 + CH_3BH_2 \rightarrow B(CH_3)_3 + BH_2C(CH_3)_3$	-2.67	-38.08
CH_3BHBH_2	-90.683 43	$CH_3BHBH_2 + CH_3BH_2 \rightarrow BH_2BH_2 + BH(CH_3)_2$	-1.36	29.27[a]
$H_2BB(CH_3)_2$	-129.731 18	$(CH_3)_2BBH_2 + 2CH_3BH_2 \rightarrow BH_2BH_2 + 2BH(CH_3)_2$	-3.33	13.80[a]
$(CH_3)_2BB(CH_3)_2$	-207.827 32	$(CH_3)_2BB(CH_3)_2 + BH_2BH_2 \rightarrow 2(CH_3)_2BBH_2$	-0.20	-17.55[a]
CH_3BHNH_2	-120.537 09	$CH_3BHNH_2 + CH_3BH_2 \rightarrow BH_2NH_2 + BH(CH_3)_2$	-1.82	-38.64[a]
$(CH_3)_2BNH_2$	-159.585 72	$(CH_3)_2BNH_2 + CH_3BH_2 \rightarrow BH_2NH_2 + B(CH_3)_3$	-2.65	-54.66[a]
BH_2NHCH_3	-120.516 42	$BH_2NHCH_3 + CH_3NH_2 \rightarrow BH_2NH_2 + NH(CH_3)_2$	-1.07	-20.88[a]
$BH_2N(CH_3)_2$	-159.540 45	$BH_2N(CH_3)_2 + CH_3NH_2 \rightarrow BH_2NH_2 + N(CH_3)_3$	-5.10	-18.08[a]
$(CH_3)_2BN(CH_3)_2$	-237.632 23	$(CH_3)_2BN(CH_3)_2 + BH_2NH_2 \rightarrow (CH_3)_2BNH_2 + BH_2N(CH_3)_2$	-3.04	-46.69[a]
BH_2OCH_3	-140.345 57	$BH_2OCH_3 + CH_3OH \rightarrow BH_2OH + O(CH_3)_2$	-3.23	-61.98[a]
CH_3BHOH	-140.374 04	$CH_3BHOH + CH_3BH_2 \rightarrow BH_2OH + BH(CH_3)_2$	1.10	-87.94[a]
$(CH_3)_2BOH$	-179.423 31	$(CH_3)_2BOH + CH_3BH_2 \rightarrow BH_2OH + B(CH_3)_3$	-.67	-104.37[a]
CH_3BHOCH_3	-179.397 76	$CH_3BHOCH_3 + BH_2OH \rightarrow CH_3BHOH + BH_2OCH_3$	-0.29	-80.24[a]
$(CH_3)_2BOCH_3$	-218.446 05	$(CH_3)_2BOCH_3 + BH_2OH \rightarrow (CH_3)_2BOH + BH_2OCH_3$	-0.44	-95.84
CH_3BHF	-164.376 79	$2CH_3BHF \rightarrow CH_3BF_2 + CH_3BH_2$	-3.06	-95.47[a]
$(CH_3)_2BF$	-203.429 56	$(CH_3)_2BF + BH_2F \rightarrow 2CH_3BHF$	-1.18	-113.17[a]
$CH_3CH_2BF_2$	-302.349 26	$CH_3CH_2BF_2 + CH_3BH_2 \rightarrow CH_3BF_2 + CH_3CH_2BH_2$	0.12	-202.27
$Be(CH_3)_2$	-93.865 40	$Be(CH_3)_2 + BeH_2 \rightarrow 2HBeCH_3$	-0.44	3.70[a]
$HBeCH_2CH_3$	-93.843 73	$HBeCH_2CH_3 + CH_3CH_3 \rightarrow HBeCH_3 + CH_2(CH_3)_2$	-4.41	20.76[a]
$HBeCH(CH_3)_2$	-132.873 73	$HBeCH(CH_3)_2 + CH_3CH_3 \rightarrow HBeCH_2CH_3 + CH_2(CH_3)_2$	-3.07	18.89[a]
$HBeC(CH_3)_3$	-171.905 32	$HBeC(CH_3)_3 + HBeCH_2CH_3 \rightarrow 2HBeCH(CH_3)_2$	0.99	16.04[a]
$CH_3BeC(CH_3)_3$	-210.954 80	$CH_3BeC(CH_3)_3 + HBeCH_3 \rightarrow Be(CH_3)_2 + HBeC(CH_3)_3$	0.06	-1.61[a]
CH_3BeBeH	-69.428 77	$CH_3BeBeH + BeH_2 \rightarrow HBeBeH + CH_3BeH$	-0.08	70.46[a]
$CH_3BeBeCH_3$	-108.478 33	$CH_3BeBeCH_3 + HBeBeH \rightarrow 2CH_3BeBeH$	-0.25	52.78[a]
CH_3BeBH_2	-80.047 43	$CH_3BeBH_2 + CH_3BeH \rightarrow HBeBH_2 + Be(CH_3)_2$	0.23	54.03[a]
$HBeBHCH_3$	-80.045 58	$HBeBHCH_3 + CH_3BH_2 \rightarrow HBeBH_2 + BH(CH_3)_2$	-1.88	56.21
$HBeB(CH_3)_2$	-119.092 97	$HBeB(CH_3)_2 + CH_3BH_2 \rightarrow HBeBH_2 + B(CH_3)_3$	-1.60	41.04[a]
$CH_3BeB(CH_3)_2$	-158.142 47	$CH_3BeB(CH_3)_2 + HBeBH_2 \rightarrow CH_3BeBH_2 + HBeB(CH_3)_2$	-0.15	21.49[a]
CH_3BeNH_2	-109.898 38	$CH_3BeNH_2 + HBeCH_3 \rightarrow HBeNH_2 + Be(CH_3)_2$	-0.55	-15.26[a]
$HBeNHCH_3$	-109.873 50	$HBeNHCH_3 + NH_2CH_3 \rightarrow HBeNH_2 + NH(CH_3)_2$	-3.38	6.24[a]
$HBeN(CH_3)_2$	-148.895 71	$HBeN(CH_3)_2 + NH_2CH_3 \rightarrow HBeNH_2 + N(CH_3)_3$	-8.55	10.18[a]
$CH_3BeN(CH_3)_2$	-187.943 97	$CH_3BeN(CH_3)_2 + HBeNH_2 \rightarrow HBeN(CH_3)_2 + CH_3BeNH_2$	-0.15	-6.71[a]
CH_3BeOH	-129.754 47	$CH_3BeOH + CH_3BeH \rightarrow HBeOH + Be(CH_3)_2$	-0.08	-76.85[a]
$HBeOCH_3$	-129.731 90	$HBeOCH_3 + CH_3OH \rightarrow HBeOH + O(CH_3)_2$	-1.65	-53.51[a]
CH_3BeOCH_3	-168.780 44	$CH_3BeOCH_3 + HBeOH \rightarrow CH_3BeOH + HBeOCH_3$	-0.45	-70.57[a]
CH_3BeF	-153.777 98	$CH_3BeF + HBeCH_3 \rightarrow Be(CH_3)_2 + BeHF$	0.91	-97.47[a]
CH_3CH_2Li	-86.041 10	$CH_3CH_2Li + CH_3CH_3 \rightarrow CH_3Li + CH_2(CH_3)_2$	-5.86	26.16[a]
$(CH_3)_2CHLi$	-125.070 95	$(CH_3)_2CHLi + CH_3CH_3 \rightarrow CH_3CH_2Li + CH_2(CH_3)_2$	-3.17	24.39[a]
$(CH_3)_3CLi$	-164.102 78	$(CH_3)_3CLi + CH_3CH_2Li \rightarrow 2LiCH(CH_3)_2$	1.25	21.37[a]
CH_3BeLi	-61.659 35	$CH_3BeLi + CH_3BeH \rightarrow HBeLi + Be(CH_3)_2$	0.43	57.75[a]
CH_3BHLi	-72.254 42	$CH_3BHLi + CH_3BH_2 \rightarrow BH_2Li + BH(CH_3)_2$	-4.02	54.49[a]
$(CH_3)_2BLi$	-111.301 70	$(CH_3)_2BLi + CH_3BH_2 \rightarrow BH_2Li + B(CH_3)_3$	-5.69	39.31[a]
CH_3NHLi	-102.064 16	$CH_3NHLi + CH_3NH_2 \rightarrow NH_2Li + NH(CH_3)_2$	-4.28	13.57[a]
$(CH_3)_2NLi$	-141.092 37	$(CH_3)_2NLi + CH_3NH_2 \rightarrow NH_2Li + N(CH_3)_3$	-5.68	13.92[a]
CH_3OLi	-121.931 55	$CH_3OLi + CH_3OH \rightarrow HOLi + O(CH_3)_2$	-0.67	-51.11[a]

[a] ΔH_f used for calculating the bond energies (see text).

a previous work, we consider the following bond terms: $E(XY)$ for each multiplicity of the XY bond, where X and Y stand for a heavy atom and $E(XH)_n{}^Y$ for XH single bonds. The subscript n is an integer depending on the number of adjacent XH bonds; for CH bonds, it may be replaced by the characters p, s, or t when respectively n = 3, 2, or 1. The superscript Y corresponds to the occurrence of one XY bond adjacent to the XH bond; when

Table V. Comparison between ΔH_f(exptl) and ΔH_f Obtained as a Sum of Bond Energies (kcal/mol)[a]

compds	ΔH_f (from $\sum E_b$)	ΔH_f(exptl)
$B(CH_3)_3$	−29.19	−29.3[b]
$B(CH_2CH_3)_3$	−36.60	−36.5,[c] −36.4,[d] −37.7,[b] −41.9[e]
B(*n*-propyl)$_3$	−51.62	−51.61,[b] −56.4,[f] −63.7[e]
B(*n*-butyl)$_3$	−66.64	−68.1,[d] −67.7,[b] −69.5[f]
B(*n*-hexyl)$_3$	−96.68	−96,[d] −94.4[g]
B(*n*-heptyl)$_3$	−111.70	−110.6,[d] −108.7[g]
B(*n*-octyl)$_3$	−126.72	−125.7,[d] −123[g]
$B(CH(CH_3)_2)_3$	−46.18	−56.7,[b] −60.1[f]
$B(CH_2CH(CH_3)_2)_3$	−71.28	−73.8,[b] −67,[d] −77.3[f]
$B(CH(CH_3)CH_2CH_3)_3$	−61.20	−60.7,[d] −58[k]
$B(CH_2CH_2CH(CH_3)_2)_3$	−86.30	−91.1[f]
$B(CH(CH_3)(CH_2)_4CH_3)_3$	−121.28	−122.7,[d] −121.4[g]

[a] All other footnotes from ref 2. [b] Johnson, W. H.; Kilday, M. V.; Prossen, E. J. [c] Cox, J. D.; Pilcher, D. [d] Pope, A. E.; Skinner, H. A. [e] Rosenblum, L. [f] Galchenko, G. L.; Varushchenko, R. M. [g] Bennett, G. E.; Skinner, H. A. [h] Haseley, E. A.; Garrett, A. B.; Sisler, H. H.

Y stands for C, the superscript is omitted.

First, we select a set of enthalpies both from theory and experiment: from MP4/6-311++G(3df,2p), we retain $\Delta H_f(BH_3)$ and $\Delta H_f(CH_3BH_2)$; from HF/6-31G*, $\Delta H_f(BH(CH_3)_2)$, $\Delta H_f(BH_2CH_2CH_3)$, $\Delta H_f(BH_2CH(CH_3)_2)$, and $\Delta H_f(BH_2C(CH_3)_3)$; and from Cox and Pilcher,[2] $\Delta H_f(B(CH_3)_3)$, $\Delta H_f(B(CH_2CH_3)_3)$, and $\Delta H_f(B(CH_2CH_2CH_3)_3)$.

If we use the CC and CH bond energies previously obtained[43] (namely, in kcal/mol, $E_b(CC) = 85.44$, $E_b(CH)_p = 98.27$, $E_b(CH)_s = 97.53$, $E_b(CH)_t = 96.86$), we can write a set of nine equations with seven unknown parameters. The least-squares fit techniques give the following values (in kcal/mol): $E_b(BC) = 77.17$, $E_b(CH)_p{}^B = 101.66$, $E_b(CH)_s{}^B = 101.35$, $E_b(CH)_t{}^B = 101.14$, $E_b(BH)_3 = 89.62$, $E_b(BH)_2 = 89.74$, and $E_b(BH)_1 = 89.92$. The correlation coefficient is close to 1, and the largest deviation between ΔH_a and $\sum E_b$ does not exceed 0.3 kcal/mol. If we apply this bond energy scheme (relation 5) to the estimation of the enthalpies of formation of a set of trialkylboranes, one obtains the values listed in Table V. For such compounds, the stabilization energy is expected to be negligible. Using this assumption, one finds that the sum of bond energies furnishes heats of formation that compare nicely to Skinner's of Johnson's results (as given by Cox and Pilcher[2]). Nevertheless, one result is surprising. Triisopropylborane has a theoretical enthalpy of formation 10 kcal/mol higher than the known experimental value. However, when we consider the series of molecules from trimethyl- to tri-*n*-octylborane, we can write

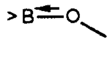
$$\Delta H_f(B((CH_2)_nCH_3)_3) = -22.25 - 4.859(3n) \qquad (6)$$

Each CH_2 group decreases the enthalpy of formation by 4.86 kcal/mol (this compares with the usual value of −4.95 kcal/mol deduced from the hydrocarbons). If we remove three CH_2 groups from $B(CH(CH_3)CH_2CH_3)_3$, $B(CH(CH_3)_2)_3$ remains. According to the slope of relation 6, the heat of formation must be increased by 14.6 kcal/mol and one obtains $\Delta H_f(B(CH(CH_3)_2)_3) = -46.6$ kcal/mol. This value is close to the sum of the bond energies and does not at all correspond to Johnson's result. For $B(CH_2CH(CH_3)_2)_3$, the sum of the bond energies gives a value (i.e., −71 kcal/mol) close to the average between Skinner's result and the value reported by Johnson. With −71 kcal/mol for $B(CH_2CH(CH_3)_2)_3$, one finds −86 kcal/mol for $B(CH_2CH_2CH(CH_3)_2)_3$, which has three additional CH_2 groups. According to this discussion, it appears that a simple additive bond energy model is quite useful to analyze consistency in a large set of enthalpies of formation and to find, eventually, inaccurate or at least surprising values.

The Remaining Bond Energies

Let us now generalize the previous approach. To determine the remaining bond energies, we have just enough compounds to build a system of equation that has as many terms as the number of unknown bond energies. The selected derivatives are quoted in Table IV, and the reference bond energies for compounds involving only H, C, N, O, and F atoms[43] are given in Table VI. The same table also contains the new standard energies for bonds involving Li, Be, and B atoms. We observe regularities in the evolution of the bond energies. The weakest value (21 kcal/mol) corresponds to the C–Li single bond and the strongest (157 kcal/mol) to the bonds that involve the fluorine atom, on the one hand, and the beryllium or the boron atom, on the other hand. Single bonds between atoms with half-filled valence shells (i.e., C–C) have an intermediate strength (85 kcal/mol). The BeH and BH bonds exhibit similar energies, independent of the nature of the adjacent bonds. More sensitive to the neighborhood are the other XH bonds. From Table VI, one calculates the following average values (and standard deviations): $E_b(BeH) = 71.3$ (±0.6), $E_b(BH) = 90.5$ (±1.2), $E_b(CH) = 98.7$ (±3.2), $E_b(NH) = 91.8$ (±2.8), and $E_b(OH) = 108.2$ (±3.2) (in kcal/mol).

Finally, let us use the bond-energy model to perform some additional comparisons with available experimental data. $(n\text{-}C_4H_9)_2BOH$ should have a negligible stabilization energy. Using its experimental heat of formation (−131.3 ± 2 kcal/mol[2] in gas phase) and the E_b from Table VI, one obtains a SE of 2.04 ± 2 kcal/mol, which seems quite acceptable. In polysubstituted molecules, the SE is no longer vanishing. For hydroxy- and alkoxyboranes, we observe the following stabilization energies[44] (in kcal/mol): $SE(BH_2OH) = -0.7$, $SE(BH_2OCH_3) = 0.2$, $SE(BH(OH)_2) = -9.4$, $SE(BH(OCH_3)_2) = -7.8$, $SE(B(OH)_3) = -15.2$, $SE(B(OCH_3)_3) = -13.1$, and $SE(B(OCH_2CH_3)_3) = -12.2$. All these polysubstituted compounds are destabilized. The destabilization depends chiefly on the number of substituents OR. The SE values are weakly sensitive to the nature of the group R. The destabilization behavior is not surprising and can be understood in terms of electronic structure. In BH_2OH, we are authorized[6] to consider the BO bond as a σ bond augmented with a π dative bond from the oxygen to the boron atom:



When the boron atom has two oxygen-containing substituents, the vacancy on the boron atom is not sufficient to permit two such simultaneous π dative bonds. Besides, such a π dative bond takes place from an electronegative atom to an electropositive one. Then, the electronic structure is an intermediate between the following resonance formulas:

The bond length increases and the bond energy decreases compared to the monosubstituted compound.

Turning our attention to difluoroborane, we observe an unexpected large stabilization energy for $CH_3CH_2BF_2$ when

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(43) Leroy, G.; Sana, M.; Wilante, C.; Van Zieleghem, M. J. *J. Mol. Struct.: THEOCHEM*, in press.

(44) According to relations from ref 43, we write $E_b(XH)_n{}^{X_2} = E_b(XH)_n + 2\Delta(XH)_n{}^X$ where $\Delta(XH)_n{}^X = E_b(XH)_n{}^X - E_b(XH)_n$.

Table VI. Standard Bond Energies (kcal/mol)[a]

X	$E_b(XH)$	$E_b(XLi)$	$E_b(XBe)$	$E_b(XB)$	$E_b(XC)$	$E_b(XN)$	$E_b(XO)$	$E_b(XF)$
H	104.21							
Li	56.57	24.55						
Be	71.38	20.89	28.35					
B	89.74	24.13	44.45	68.29				
C	98.27	30.04	55.46	77.17	*85.44*			
N	91.54	58.03	81.16	105.94	*76.59*	*50.54*		
O	108.03	97.08	119.03	129.92	*91.66*	*52.42*	*45.88*	
F	136.22	138.50	157.01	157.52	*116.26*	*65.86*	*47.76*	*37.95*

X	$E_b(BeH)_1^X$	$E_b(BH)_1^X$	$E_b(BH)_2^X$	$E_b(CH)_t^X$	$E_b(CH)_s^X$	$E_b(CH)_p^X$	$E_b(NH)_1^X$	$E_b(NH)_2^X$	$E_b(OH)_1^X$
Li	70.95	91.48	92.36	101.74	102.36	103.47	91.82	94.41	108.65
Be	71.30	91.50	90.39	101.90	102.39	103.00	95.59	95.92	110.05
B	71.31	91.19	90.99	101.14	101.35	101.66	94.45	95.64	111.55
C	71.38	89.92	89.74	*96.86*	*97.53*	*98.27*	*90.54*	*91.54*	*108.03*
N	72.08	90.64	92.36	*95.97*	*96.07*	*96.85*	*89.23*	*90.24*	*107.50*
O	71.92	90.24	89.36	*94.86*	*95.48*	*95.87*	*88.88*	*89.51*	*105.12*
F	70.38	88.96	88.37	*95.04*	*95.20*	*95.44*	*88.85*	*88.59*	*103.84*

[a] Italic values are taken from ref 43.

the experimental enthalpy of formation is employed (−209 kcal/mol[37]). This surprising result seems to derive from an unrealistic experimental value. Indeed, if we add one CH_2 group to CH_3BF_2, its heat of formation should be changed according to

$$\Delta H_f(\mathrm{C}) + 2\Delta H_f(\mathrm{H}) = 3[E_b(\mathrm{CH})_p - E_b(\mathrm{CH})_p{}^{\mathrm{B}}] + E_b(\mathrm{CC}) + 2E_b(\mathrm{CH})_s{}^{\mathrm{B}} = -2.5 \text{ kcal/mol}$$

Assuming equal SE values for $BF_2CH_2CH_3$ and BF_2CH_3, we expect an enthalpy of formation close to −201.5 kcal/mol for ethyldifluoroborane, instead of −209 kcal/mol. The isodesmic procedure confirms this result, leading to −202.2 kcal/mol (see Table IV). It must be noted that the isodesmic approach makes use of the CH_3BF_2 heat of formation. However, the experimental value we have retained for this compound does not seem to be questionable. The following isodesmic reaction confirms the experimental value of −199 kcal/mol for methyldifluoroborane: $CH_3BF_2 + CH_3BH_2 \rightarrow BHF_2 + BH(CH_3)_2$. Similarly, one expects a $\Delta H_f(BF_2CH(CH_3)_2)$ only 3.2 kcal/mol lower than the $\Delta H_f(BF_2CH_2CH_3)$. This gives −205.5 kcal/mol instead of −212 kcal/mol.[37]

Finally, the isodesmic approach leads to large heats of formation for alkyllithium compared with the experimental quantities. This in a consequence of the value reported in Table I for methyllithium. Lebedev et al.[45] give an experimental estimate of the gas-phase heats of formation for ethyl- and the *n*-butyllithium: 13.9 and 6.4 kcal/mol, respectively, against 27.8 and 17.7 from Table IV. Including $\Delta H_f(CH_3Li,gas)$ from ref 2, one observes that both sets correlate ($\Delta H_f(\text{exp, gas}) = -44.405 + 2.205$, $\Delta H_f(\text{th, gas})$ in kcal/mol with $\rho = 0.955$). Nevertheless, large differences exist between individual terms (from 10 to 25 kcal/mol). This may originate in the difficulties to obtain accurate (and reproducible[46]) heats of sublimation. It has been shown that alkyllithium compounds are associated in the vapor phase.[47,48] Gaseous ethyllithium consists of tetramer and hexamer molecules, and the related association energies are expected to be large.[49] Nevertheless, experimental heats of formation of lithium derivatives in the condensed state correlate in a satisfactory manner with our theoretical gas-phase estimates (see Table VII). The regression equation between both sets is

$$\Delta H_f(\text{th, gas}) = 34.71 + 0.616\Delta H_f(\text{exptl, condensed phase}) \text{ kcal/mol} \quad (\rho = 0.940) \quad (7)$$

Table VII. Comparison between Experimental and Theoretical Enthalpies of Formation of Alkyllithium Compounds (Values in kcal/mol)

compds	ΔH_f(exptl, condensed phase)	ΔH_f(th, gas phase)	ΔH_f(using relation 7)
CH_3Li	-17 ± 0.5^a	25.23	24.24
	-17.9^b		23.69
CH_3CH_2Li	-14 ± 1.3^c	26.16	26.09
	-12.67 ± 0.5^a		26.91
	-13.2^b		26.58
$CH_3CH_2CH_2Li$	$(-21.81)^d$	21.15^f	21.28
$(CH_3)_2CHLi$	-17.8 ± 0.5^a	24.86	23.75
	-17.6^e		23.87
$CH_3CH_2CH_2CH_2Li$	-32 ± 1.7^c	16.14^f	15.00
	-31.21 ± 0.67^b		15.49
	-26.1^a		18.64
$CH_3CH_2CH(CH_3)Li$	$-21 \pm 0.5^{a,b}$	18.75^f	21.78
$(CH_3)_3CLi$	-22^a	21.37	21.16

[a] Reference 50. [b] Reference 51. [c] Reference 45. [d] Predicted value, using relation 7. [e] Corrected value of ref 51 according to relation 2 of this reference. [f] From $\sum E_b$, assumins SE = 0.

The quantities listed in Table VII suggest also that the thermal effect for going from condensed phase to monomeric gas phase can be as large as 42–49 kcal/mol.

Conclusions

Given the problems that can arise to measure or to calculate the enthalpies of formation in lithium, beryllium, and boron chemistry, it is interesting to obtain a consistent set of accurate ΔH_f values. The theoretical values we propose in this work reproduce most of the experimental quantities in a quite satisfactory manner. Large discrepancies seem to correspond to unrealistic experimental data. However, no theoretical or experimental evidence exists to support this assertion. For $B(CH(CH_3)_2)_3$, $B(CH_2CH_2CH(CH_3)_2)_3$, $BF_2CH_2CH_3$, $BF_2CH(CH_3)_2$, and $LiCH_3$, we propose alternative theoretical values. We believe that the most accurate theoretical values (Table I) fall into the

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"chemical precision". Isodesmic results may exhibit slightly larger errors. However, it should be noted that the results also depend on the atomic data for Li, Be, and B. Finally, the selected heats of formation have been used to build a table of standard bond energies useful for studying the stability of the chemical species.

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The Chemistry of (ring)Ru^{2+} (ring = Tetramethylthiophene, *p*-Cymene)

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Described are the compounds $[(\text{ring})\text{Ru}(\text{OTf})_2]_x$, where ring = 2,3,4,5-tetramethylthiophene (TMT, **1**), and *p*-cymene (**2**). These electrophilic reagents serve as precursors to $[(\text{ring})\text{RuL}_3]^{2+}$, where $L_3 = (H_2O)_3$, $(NH_3)_3$, and $(PH_3)_3$. Solutions of **1** and **2** react with carbon monoxide to give $(\text{ring})\text{Ru}(\text{CO})(\text{OTf})_2$. The addition of thiophenes to CH_2Cl_2 solutions of **1** or **2** leads to the precipitation of the sandwich compounds $[(\text{ring})(SC_4R_4)\text{Ru}](\text{OTf})_2$, where SC_4R_4 = thiophene, 2,5-dimethylthiophene, and TMT. $[(\text{TMT})\text{Ru}(H_2O)_3](\text{OTf})_2$ was characterized by single-crystal X-ray crystallography, which established a piano-stool geometry with a planar TMT ligand. $[(\text{TMT})\text{Ru}(D_2O)_3](\text{OTf})_2$ decomposes in D_2O solution at 150 °C to give $[(\text{TMT})_2\text{Ru}]^{2+}$, which undergoes selective deuteration at the 2,5-methyl groups. D_2O solutions of $[(\text{TMT})_2\text{Ru}]^{2+}$ undergo photochemical loss of one TMT ligand in water to give $[(\text{TMT})\text{Ru}(D_2O)_3]^{2+}$. Photolysis of an aqueous solution of $[(\text{TMT})(p\text{-cymene})\text{Ru}]^{2+}$ gives primarily $[(\text{TMT})\text{Ru}(H_2O)_3]^{2+}$. A procedure is described for the reversible loading of **1** onto γ-alumina, which in turn was characterized by ^{13}C CP-MAS NMR spectroscopy.

Introduction

The chemistry of metal thiophene complexes is a topical area of research that is progressing very rapidly.[1-5] This trend is partly due to interest in a molecular level understanding of metal-catalyzed thiophene desulfurization. More fundamentally, however, little is known about the basic coordination chemistry of thiophenes. One of our recent contributions to this area centered on the synthesis of $[(\text{TMT})\text{RuCl}_2]_2$, the first thiophene complex with replaceable coligands[6] (TMT is 2,3,4,5-tetramethylthiophene).

In the present contribution we describe the chemistry of $[(\text{TMT})\text{Ru}(\text{OTf})_2]_x$ (OTf = O_2SCF_3), a reagent that serves as a source of (TMT)Ru^{2+}. This reagent has permitted us to prepare a range of new thiophene complexes bearing a variety of coligands. The catalysts used commercially for fossil fuel desulfurization consist of transition-metal compounds dispersed on an oxide support, typically alumina. We therefore sought to develop the chemistry of (TMT)Ru^{2+} bound to oxygen ligands. We have investigated the corresponding chemistry of (arene)Ru^{2+} in the form of $[(p\text{-cymene})\text{Ru}(\text{OTf})_2]_x$ (*p*-cymene is 4-isopropyltoluene).

Results

$[(\text{TMT})\text{RuCl}_2]_2$ can be prepared in 80% yield in one step from TMT and the commercially available $[(p\text{-cymene})\text{RuCl}_2]_2$. TMT can be prepared in a two-step procedure from 2,5-dimethylthiophene, which can also be purchased in bulk. Unsuccessful attempts were made to prepare the Os and Fe analogues of $[(\text{TMT})\text{RuCl}_2]_2$, in the first instance by an exchange reaction with $[(p\text{-cymene})\text{OsCl}_2]_2$ and in the second case by the reaction of anhydrous FeCl_2 with refluxing TMT. The thermal exchange reaction of 2,5-dimethylthiophene and $[(p\text{-cymene})\text{RuCl}_2]_2$ was also unsuccessful.

Synthesis and Properties of $[(\text{TMT})\text{Ru}(\text{OTf})_2]_x$. This compound was prepared by the straightforward reaction of a dichloromethane solution of $[(\text{TMT})\text{RuCl}_2]_2$ with silver trifluoromethanesulfonate (AgOTf). The resulting orange solution is filtered and treated with hexane to give an orange solid. Because we were primarily interested in using this compound as a synthetic intermediate, its structure was not of specific interest. Triflate ligands can bind to one or more metals in a variety of ways,[7] and the spectral data suggest that $[(\text{TMT})\text{Ru}(\text{OTf})_2]_x$ may not have a simple structure. In CD_2Cl_2 its ^{1}H NMR spectrum consists of three pairs of methyl resonances in the ratio of 1.5:1.5:1.0:0.3:1.0:0.3. In CD_3NO_2, however, the ^{1}H NMR spectrum consisted of two singlets, indicating either a dynamic process or a single ionic species. On the basis of IR absorptions[7] in the ν_{SO} region both OTf$^-$ anions are thought to be coordinated in the solid state (Figure 1). This assignment rests on the previously noted[7]

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