

## *Ab Initio* UHF Calculations

Part 7.—Possible Evidence for Environmental Effects on the Radicals  
 $\text{BH}_3^-$ ,  $\text{CH}_3$  and  $\text{NH}_3^+$

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The radicals  $\text{BH}_3^-$ ,  $\text{CH}_3$  and  $\text{NH}_3^+$  are compared using *ab initio* UHF calculations after annihilation of the contaminating quartet spin state. Although there is a consistency in the trends predicted for the properties, these are not in accord with those determined experimentally. Although the out-of-plane zero-point energy vibration has a dominating influence, it is concluded that the environment must determine the physical properties of  $\text{BH}_3^-$ .

In calculations using a minimal basis set of orbitals there is always the possibility that the wave functions are inadequately described and a source of any discrepancy between theory and experiment. It is therefore important to compare calculations on systems with analogous sets of basis orbitals. This is not necessarily a sufficient criterion because, e.g., in  $\text{F}_2^-$  the number of electrons is so large that only doublet state wave functions can be constructed if a minimal basis set of orbitals is used, whereas for CN all possible states up to the octet state can be constructed. Therefore it is not to be unexpected if UHF calculations on these two systems do not give results which compare equally well with experiment. On the other hand, if a series of radicals which have analogous sets of basis orbitals, and are also isoelectronic, are studied, one would expect the results to compare equally well with experiment.

The radicals  $\text{BH}_3^-$ ,  $\text{CH}_3$  and  $\text{NH}_3^+$  form an isoelectronic series with analogous minimal basis sets of orbitals, so if we obtain agreement with experiment for a calculation on one of the radicals the other two should also agree. However, these radical species possess different charges. Charged species are expected to interact more strongly with their immediate environment than neutral species. Therefore, this series of radicals should be useful in providing information on the effect of the environment on hyperfine coupling constants in e.s.r. spectra. This paper considers *ab initio* UHF calculations on the  $\text{BH}_3^-$  anion after establishing the agreement (in more than one aspect) between theory and experiment for  $\text{CH}_3$  and  $\text{NH}_3^+$ .

Experimentally these radicals have been subject to many investigations.<sup>1-8</sup> All the radicals have been assumed generally to be planar,<sup>2</sup> having very similar *U*-values.<sup>9</sup> It is thought that out-of-plane vibrations are responsible for augmenting the heavy atom isotropic coupling constants in  $\text{CH}_3$ <sup>10-12</sup> and  $\text{NH}_3^+$ ,<sup>13</sup> although other explanations have been proposed.<sup>14-16</sup>

### METHOD

The *ab initio* UHF method in the LCAO—MO approximation with spin annihilation,<sup>17</sup> as described previously<sup>18</sup> was used. The minimal basis set of orbitals was represented by expansions of gaussian functions in their completely contracted form ;

9 *s*-type and 5 *p*-type for nitrogen, carbon and boron, and 6 *s*-type for hydrogen as given by Huzinaga.<sup>19</sup> The orbital exponent  $\alpha$  of the hydrogen atomic orbital and the bond length  $r(\text{X—H})$  were both optimized (see e.g., fig. 1 of ref. (13)) to an accuracy of 0.05, assuming in each case that the radical was planar. All the results were calculated from the UHF wavefunction after annihilation of the contaminating quartet spin state<sup>12</sup> and are expressed in atomic units (a.u.) except for the hyperfine coupling constants which are expressed in G ( $10 \text{ G} \equiv 1 \text{ mT}$ ). Non-planar nuclear configurations were studied by moving the heavy atom perpendicularly out of the plane of the three fixed hydrogen atoms. The anisotropic coupling constants were evaluated according to the method described elsewhere.<sup>20</sup>

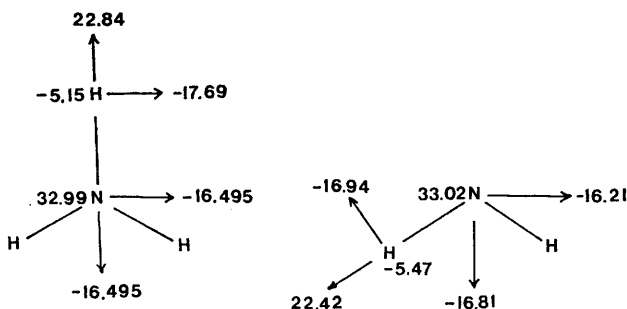


FIG. 1.—Anisotropic coupling constants for the radicals  $\text{NH}_3^+$  and  $\text{NH}_2$ .

#### AMMONIA RADICAL CATION

Hyde and Freeman<sup>8</sup> and Cole<sup>7</sup> have observed electron spin resonance spectra from X-ray irradiated ammonium perchlorate crystals at room temperature which were interpreted to arise from the radical ion  $\text{NH}_3^+$  with isotropic hyperfine coupling constants,  $a(^{14}\text{N}) = 18.1 \text{ G}$ ,  $a(^1\text{H}) = 25 \text{ G}$ <sup>7</sup> and  $a(^{14}\text{N}) = 19.3 \text{ G}$ ,  $a(^1\text{H}) = 25.8 \text{ G}$ .<sup>8</sup> Rao and Symons<sup>14</sup>  $\gamma$ -irradiated ammonium perchlorate and obtained the same radical with  $a(^{14}\text{N}) = 19.3 \text{ G}$ ,  $a(^1\text{H}) = 25.8 \text{ G}$  at room temperature and at 77 K. The hyperfine coupling constants have been calculated using the *ab initio* UHF method, after optimization of the geometry and hydrogen atomic orbital exponent, for the planar radical to be  $a(^{14}\text{N}) = 10.57 \text{ G}$ ,  $a(^1\text{H}) = -22.65 \text{ G}$ .<sup>13</sup> Allowing for the out-of-plane zero point energy vibration, the calculated coupling constants were modified to  $a(^{14}\text{N}) = 16.92 \text{ G}$ ,  $a(^1\text{H}) = -20.02 \text{ G}$ . In addition, the anisotropic coupling constants  $B$  are given in fig. 1. These are similar to those for  $\text{NH}_2$  (also fig. 1) giving  $A_{\parallel}(^{14}\text{N}) = 41.66 \text{ G}$ ,  $A_{\perp}(^{14}\text{N}) = -8.05 \text{ G}$  which compare favourably with experimental<sup>14</sup>;  $A_{\parallel}(^{14}\text{N}) = 41.7 \text{ G}$ ,  $A_{\perp}(^{14}\text{N}) = 0 \pm 3 \text{ G}$ . The anisotropic coupling constants can be calculated far more reliably than isotropic coupling constants and therefore we should be able to give equally good estimates for the  $A$  values as we have for the  $a$  values. Since the calculated  $a(^{14}\text{N})$  is low by only 2.3 G compared with experiment, the discrepancies between the calculated and experimental  $A$  values should not be any larger than this. The calculated values are  $A_{\parallel}(^{14}\text{N}) = 50 \text{ G}$ ,  $A_{\perp}(^{14}\text{N}) = 0.5 \text{ G}$ , whereas experimentally  $A_{\parallel}(^{14}\text{N}) = 37 \text{ G}$ ,  $A_{\perp}(^{14}\text{N}) = 10.5 \text{ G}$ . The large discrepancies are associated with the fact that the true  $A_{\parallel}$  and  $A_{\perp}$  values are not measured but have been partially averaged by a librational motion of the three-fold molecular axis.<sup>14</sup> (If we had used the expression<sup>21</sup>  $A(\text{estimated}) = a(\text{experimental}) + B(\text{calculated})$  the discrepancies would have been even larger). The calculated anisotropy of the proton coupling constants (fig. 1) is never completely observed owing to a rapid rotation about the three fold axis so we should use

$B_{\perp} = 0.5(B_x + B_y) = 2.575$  G giving a calculated difference between  $A_{\parallel}({}^1\text{H})$  and  $A_{\perp}({}^1\text{H})$  of 7.725 G. The observed difference is only 3.3 G.<sup>14</sup> The discrepancy can also be associated with the librational motion already discussed. Generally, the agreement between theoretical and experimental values is satisfactory and with the exception of the vibrations and rotations discussed above it is unnecessary to consider any other effects at this stage.

## METHYL RADICAL

This radical has been studied in much greater detail than either of its isoelectronic counterparts, both theoretically and experimentally. An early determination by Cole *et al.*<sup>4</sup> of  $a({}^{13}\text{C}) = 41$  G was interpreted to be characteristic of a planar radical since its magnitude is relatively small. Experimentally,  $a({}^{13}\text{C}) = 38$  G and  $a({}^1\text{H}) = -23$  G<sup>22</sup> seem to be generally true in solution and matrix environments although the hyperfine coupling constants are temperature dependent. On Vycor glass below 150 K, values below  $a({}^{13}\text{C}) = 38$  G have been measured which have been extrapolated to obtain  $a({}^{13}\text{C}) = 10.6$  G at 0 K.<sup>23</sup>

Calculations have predicted reasonable values for the proton hyperfine coupling constant,<sup>24</sup> but high values for  $a({}^{13}\text{C})$ .<sup>25, 30, 31</sup> The emphasis in most empirical and semi-empirical calculations has been on the importance of an out-of-plane vibration on the hyperfine coupling constants, a suggestion of Schrader and Karplus.<sup>10</sup>

TABLE 1.—THEORETICAL RESULTS FOR THE METHYL RADICAL

bond length (a.u.)	hydrogen orbital exponent	angle of bending	total energy (a.u.)	hyperfine coupling constants (G)	
				$a({}^1\text{H})$	$a({}^{13}\text{C})$
2.00	1.35	0	-39.538 2	-21.52	27.35
2.05	1.35	0	-39.541 6	-22.42	28.78
2.10	1.35	0	-39.541 3	-23.41	30.27
2.00	1.40	0	-39.540 9	-22.46	25.96
2.05	1.40	0	-39.542 8	-23.39	27.33
2.10	1.40	0	-39.541 1	-24.42	28.74
2.00	1.45	0	-39.541 0	-23.30	24.63
2.05	1.45	0	-39.541 5	-24.25	25.91
2.10	1.45	0	-39.538 2	-25.28	27.23
2.05	1.40	2	-39.542 7	-23.21	28.68
2.05	1.40	5	-39.542 2	-22.13	35.44
2.05	1.40	10	-39.539 8	-18.84	57.85
2.05	1.40	20	-39.526 0	-10.61	128.3
2.05	1.40	30	-39.490 8	-5.435	212.5
anisotropic coupling constants (G)					
			$B_{\parallel}({}^{13}\text{C})$	$B_{\parallel}({}^1\text{H})$	
2.05	1.40	0	62.52	-1.93	
2.05	1.40	5	61.77	-2.01	

The temperature dependence above 150 K is well explained by including the effects of this vibration.<sup>11, 12</sup> Below 150 K, Symons and Rao<sup>14</sup> have suggested that Garbutt *et al.*<sup>23</sup> have misinterpreted the spectrum and are really measuring  $A_{\perp}({}^{13}\text{C})$  rather than  $a({}^{13}\text{C})$ . It is estimated, after taking into account the out-of-plane zero-point energy vibration, that the anisotropic coupling constant is  $B_{\perp}({}^{13}\text{C}) = -30$  G, from the results in table 1. If Symons and Rao<sup>14</sup> are correct, and the minimum possible value for  $a({}^{13}\text{C})$  is 38 G, then  $A_{\perp}({}^{13}\text{C}) \sim 8$  G. This compares favourably with the value obtained by Garbutt *et al.*<sup>23</sup> after extrapolation to 0 K. Our reasons

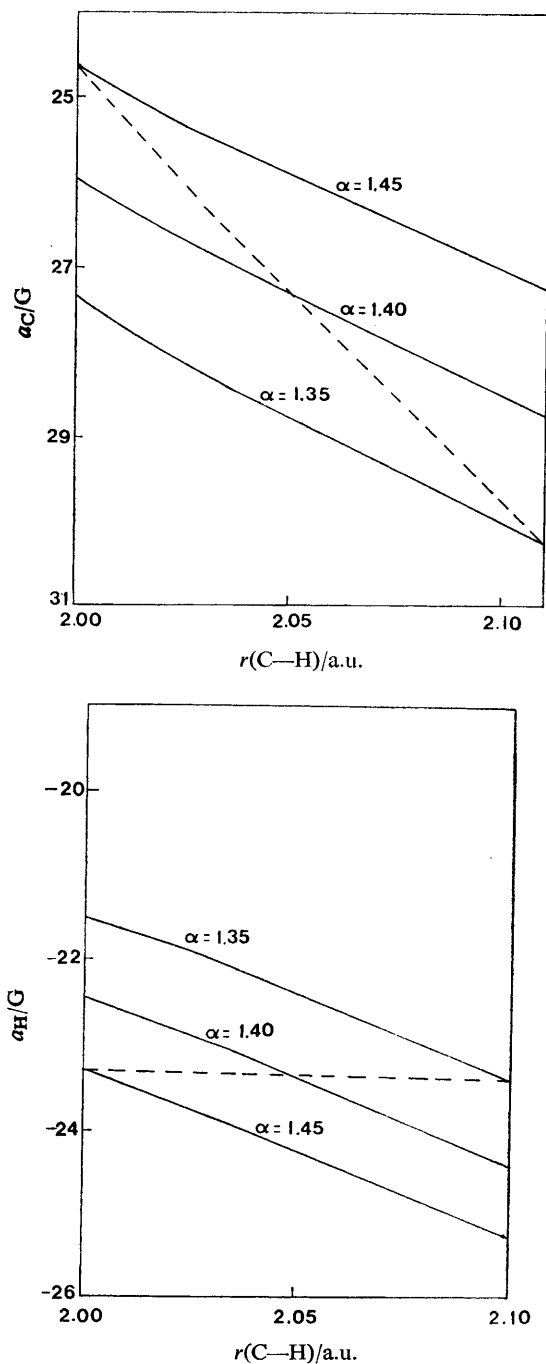


FIG. 2.— —, variation of the carbon and hydrogen hyperfine coupling constants with bond distance for those values of the hydrogen atomic orbital exponent,  $\alpha$ , which have been indicated. ---, estimated variation of the carbon and hydrogen hyperfine constants with bond distance at minimum total energy.

for using theoretical anisotropic coupling constants with experimental isotropic coupling constants have been discussed.<sup>22</sup> It is further justified since our value for  $B_{\perp}(^{13}\text{C})$  is close to that calculated for an atomic Hartree-Fock  $2p$  distribution.<sup>21</sup> We therefore reject the unusual results of Garbutt *et al.*<sup>23</sup> by accepting this interpretation.

In the same manner, as outlined in the calculations on  $\text{NH}_3^+$ ,<sup>13</sup> the effect of the out-of-plane zero-point energy vibration has been included non-empirically, using results listed in table 1. The out-of-plane vibrational force constant has been evaluated as  $k = 0.0405$  a.u. (1 a.u. =  $1544 \text{ N m}^{-1}$ ).

This is much less than that calculated for  $\text{NH}_3^+$  ( $k = 0.1136$  a.u.), thereby explaining why there is a marked temperature dependence of the coupling constants for  $\text{CH}_3$  but not for  $\text{NH}_3^+$ . The force constant for the symmetrical stretch vibration is much higher ( $k = 1.292$  a.u.) and similar to that for  $\text{NH}_3^+$  ( $k = 1.372$  a.u.). However, it is only the out-of-plane zero point energy vibration  $a_2''$  which significantly modifies the hyperfine coupling constants.<sup>12</sup>

The increment to be added to the planar radical isotropic coupling constants to account for the out-of-plane zero-point energy vibration is 27.31 G for carbon and 3.96 G for hydrogen. Hence, the theoretical estimates at absolute zero for the observed isotropic coupling constants are  $a(^{13}\text{C}) = 27.33 + 27.31 = 54.64 \text{ G}$ ;  $a(^1\text{H}) = -23.39 + 3.96 = -19.43 \text{ G}$ . The agreement with experiment is not so good as for  $\text{NH}_3^+$  but is still reasonable. The trend of the temperature variation of both  $a(^{13}\text{C})$  and  $a(^1\text{H})$  is also correctly predicted since the effect of increasing the temperature is to increase the value of the increment to be added to the planar radical.

The predicted variations of  $a(^{13}\text{C})$  and  $a(^1\text{H})$  with bond length (in the  $a_1'$  stretching mode) are shown in fig. 2. For a given hydrogen atomic-orbital exponent the variations parallel those obtained by the INDO method.<sup>12</sup> If the optimum orbital exponent is used at each bond length,  $a(^1\text{H})$  becomes almost independent of the CH bond length whereas  $a(^{13}\text{C})$  becomes more sensitive.

#### BOROHYDRIDE ANION

This radical anion was reported by Symons and Wardale<sup>1</sup> by  $\gamma$ -irradiation of  $\text{KBH}_4$  and later<sup>2</sup> the reasons for the identification were elaborated. Better spectra have since been obtained using tetramethylammonium borohydride over a wide temperature range.<sup>3</sup> The two investigations are only in qualitative agreement in that significant differences occur in the hyperfine coupling constants;  $a(^{11}\text{B}) = 24.2 \text{ G}$ ,<sup>2</sup>  $a(^{11}\text{B}) = 20.7 \text{ G}$ ,<sup>3</sup>  $a(^1\text{H}) = 16.3 \text{ G}$ ,<sup>2</sup>  $a(^1\text{H}) = 15.1 \text{ G}$ .<sup>3</sup> This is probably an environmental effect since the hyperfine coupling constants are independent of temperature between 84 and 300 K.<sup>3</sup>

The evidence for  $\text{BH}_3^-$  is strong. It is expected from chemical considerations and is the only reasonable species to fit the e.s.r. spectrum. Comparisons of the hyperfine coupling constants with  $\text{CH}_3$  and  $\text{NH}_3^+$  are interpreted as further evidence.<sup>2</sup> The comparative success of *ab initio* UHF calculations to explain the origins of the hyperfine coupling constants of  $\text{CH}_3$  and  $\text{NH}_3^+$  should provide further evidence for the assignment of  $\text{BH}_3^-$ . The results of some of the *ab initio* UHF calculations on  $\text{BH}_3^-$  are given in table 2 and show how the total energy, after annihilation of the quartet spin state, and hyperfine coupling constants vary in the region of the energy minimum as a function of the hydrogen atomic orbital exponent  $\alpha$  the B—H bond length and the bending angle  $\theta$ .  $\text{BH}_3^-$  is calculated to be bent<sup>26</sup> out of plane by about  $9^\circ$  in contrast to the planar configurations calculated for  $\text{CH}_3$  and  $\text{NH}_3^+$ .<sup>13</sup> For this geometry,  $a(^{11}\text{B}) \sim 45 \text{ G}$ ,  $a(^1\text{H}) \sim -16.5 \text{ G}$ , the former of which is far too large.

Even for the planar configuration,  $a(^{11}\text{B})$  is too large when the contribution to the isotropic coupling constant from the out-of-plane zero-point energy vibration still has to be taken into account. It is difficult to estimate the vibrational contribution owing to the double minimum in the energy curve with out-of-plane bending<sup>26</sup> but 100 G would seem to be a conservative estimate. Also, the force constant will be less than for  $\text{CH}_3$  so that a large temperature variation in  $a(^{11}\text{B})$  would be expected, which has not been observed.<sup>3</sup>

TABLE 2.—THEORETICAL RESULTS FOR THE ISOLATED BOROHYDRIDE ANION

bond length (a.u.)	hydrogen orbital exponent	angle of bending	total energy (a.u.)	hyperfine coupling constants (G)	
				$a(^1\text{H})$	$a(^{11}\text{B})$
2.35	1.10	0	−26.321 5	−18.58	23.48
2.40	1.10	0	−26.321 6	−19.30	24.84
2.45	1.10	0	−26.320 0	−20.10	26.28
2.30	1.15	0	−26.323 0	−19.41	21.15
2.35	1.15	0	−26.323 7	−20.15	22.41
2.40	1.15	0	−26.322 5	−20.86	23.73
2.25	1.20	0	−26.320 8	−19.97	19.08
2.30	1.20	0	−26.322 4	−20.70	20.25
2.35	1.20	0	−26.321 9	−21.51	21.47
2.40	1.20	0	−26.319 6	−22.40	22.76
2.35	1.15	2	−26.323 7	−19.94	23.66
2.35	1.15	5	−26.323 9	−18.87	30.04
2.35	1.15	8	−26.324 1	−17.11	40.98
2.35	1.15	10	−26.324 1	−15.72	50.19
2.35	1.15	20	−26.319 3	−9.169	106.8
2.35	1.15	30	−26.297 9	−7.112	166.2
2.00	1.40	0	−26.269 2	−20.52	11.15
2.00	1.40	5	−26.268 7	−19.71	16.99
2.00	1.40	10	−26.266 9	−17.66	33.22
anisotropic coupling constants (G)					
			$B_{  }(^{11}\text{B})$	$B_{  }(^1\text{H})$	
2.35	1.15	0	36.49	−0.11	
2.35	1.15	5	35.86	−0.25	
2.35	1.15	10	34.23	−0.60	

The possibility that  $A_{\perp}(^{11}\text{B})$  has been measured rather than  $a(^{11}\text{B})$ , analogous to the interpretation<sup>14</sup> we have accepted for the methyl radical, can be dismissed for three reasons. First, the e.s.r. spectra<sup>2, 3</sup> are characteristically isotropic. Secondly,  $B_{\perp}(^{11}\text{B})$ , which is only slightly modified by the out-of-plane vibration (table 2), is only about −17 G and so  $A_{\perp}(^{11}\text{B})$  will only be about 17 G lower than the 120 G which has been estimated for  $a(^{11}\text{B})$ . Thirdly, the temperature variation of  $A_{\perp}(^{11}\text{B})$  would be marginally greater than that for  $a(^{11}\text{B})$ .

Some confidence in the calculations for the rigid planar radicals is given by the agreement between our theoretical  $a(^{13}\text{C})$  and the estimate given by Fessenden.<sup>22</sup> On the other hand, environmental interactions, if important, place in jeopardy the validity of the force constant calculations. If the electronic contributions are more important than the vibrational contributions or environmental effects on the hyperfine coupling constants, we would expect that the trends calculated for the rigid planar radicals should reproduce experimental trends. The proton hyperfine coupling constants increase in order  $\text{BH}_3^-$ ,  $\text{CH}_3$ ,  $\text{NH}_3^+$  (−16.5 G, −23.0 G, −25.9 G) as predicted from an excess charge effect.<sup>27, 28</sup> Although the optimized orbital

exponents (1.15, 1.4, 1.6) for the planar radicals are in the order expected from the excess charge effect, the calculated proton coupling constants are not ( $-20.15$  G,  $-23.39$  G,  $-22.65$  G). Analysis of the results (ref. (13) and tables 1 and 2) shows that the apparent randomness in the proton coupling constants arises because of the influence of two opposing trends.

(i) If we select those bond lengths which minimize the energy for each radical for a particular orbital exponent,  $\alpha = 1.4$ , a characteristic procedure of many semi-empirical methods (e.g., INDO), we would obtain respectively  $-23.21$  G,  $-22.46$  G,  $-20.04$  G, a trend in opposition to that observed experimentally.

(ii) The excess charge can be looked at in approximate isolation by comparing hyperfine coupling constants of these radicals for a standard bond length but optimized hydrogen atomic orbital exponent. From the available results we use a bond length of 2 a.u. and hydrogen atomic orbital exponents of 1.2 for  $\text{BH}_3^-$ , 1.4 for  $\text{CH}_3$  and 1.6 for  $\text{NH}_3^+$ . The respective proton coupling constants for these particular cases are  $-17.32$  G,  $-22.46$  G and  $-23.36$  G, the trend being in agreement with experiment.

TABLE 3.—THEORETICAL RESULTS FOR  $\text{BH}_3^-$  WITH AN ASSUMED ENVIRONMENT

environment	0°	angle of bending * 5°	10°
<i>a</i>	$-38.270\ 5$	$-38.269\ 9$	$-38.268\ 0$
	10.59	12.90	19.34
	$-15.29$	$-14.72$	$-13.24$
<i>b</i>	$-25.635\ 3$	$-25.635\ 5$	$-25.635\ 6$
	22.25	30.04	50.61
	$-19.97$	$-18.69$	$-15.51$
<i>c</i>	$-21.510\ 4$	$-21.510\ 5$	$-21.510\ 4$
	22.08	30.03	51.01
	$-19.79$	$-18.49$	$-15.29$
<i>d</i>	$-26.532\ 8$	$-26.533\ 0$	$-26.533\ 0$
	22.23	30.04	50.64
	$-19.95$	$-18.67$	$-15.49$
<i>e</i>	$-29.960\ 7$	$-29.960\ 8$	$-26.960\ 9$
	22.23	30.03	50.61
	$-19.95$	$-18.66$	$-15.49$

\* for a particular angle of bending the results are in order; total energy (after spin annihilation),  $a(^{11}\text{B})$ ,  $a(^1\text{H})$ .

(a) the environment is represented by an extra unit positive charge at the boron nucleus; (b) the environment is represented by six unit positive charges, i.e., the six nearest neighbours in  $\text{NaBH}_4$ ,<sup>32</sup>; (c) as in (b) except that the charges are two units; (d) as in (b) with the addition of twelve negative unit charges at the next nearest neighbour positions in  $\text{NaBH}_4$ ; (e) as in (d) with the addition of eight positive unit charges at the third nearest neighbour positions in  $\text{NaBH}_4$ .

The discrepancies between the trends observed experimentally and those calculated for the rigid planar radical imply that other effects have a dominating influence. This is further substantiated since the experimentally derived  $U$ -values for the heavy atoms of these radicals are  $2.9(^{11}\text{B})$ ,  $3.4(^{13}\text{C})$ ,  $3.5(^{14}\text{N})$ , whereas the predicted  $U$ -values from the calculations on the rigid planar radicals are 3.2, 2.4 and 1.8 respectively.

Any environmental effect will be expected to be over-emphasized in these radicals owing to the importance of the out-of-plane vibration. The usual molecular interaction forces arising from a neutral host lattice are expected to increase the force constants of the guest radical compared to the corresponding isolated radical. Super-



imposed on this effect will be an additional interaction between a lattice and radical which are both charged. In order qualitatively to obtain agreement with experiment, we have to assume that a positively charged lattice affects a negatively charged radical in such a way as to increase still further the out-of-plane vibrational force constants. In this way, the temperature independence of the  $\text{BH}_3^-$  spectrum can be explained. Since  $\text{NH}_3^+$  is relatively unpolarizable, in this respect the qualitative deduction is less critical but the implication is that a negatively charged lattice tends to decrease the out-of-plane vibrational force constant, i.e., the environmental effects are partially compensated. Some attempts at including environmental effects are now described.

The simplest, although unjustifiable, way of incorporating the effect of a positively charged environment about the  $\text{BH}_3^-$  anion is to place an extra positive charge at the boron nucleus. The results are given in table 3. Two points emerge; the radical is now planar, which is expected since we have effectively increased the boron electronegativity,<sup>29</sup> and secondly,  $a(^{11}\text{B})$  is reduced so much that even with the out-of-plane zero point energy vibration the hyperfine coupling is estimated to be reasonably close to experimental.

A more realistic model is to represent the environment by a series of point charges. A face-centred cubic lattice was chosen (unit cell size 11.64 a.u. characteristic of the sodium borohydride lattice<sup>32</sup>) with the  $\text{BH}_3^-$  ion oriented such that the three-fold axes of the lattice and radical were parallel. The results are shown in table 3 and show that the effects on the optimized isolated radical calculations are minimal. This result shows that the sodium ion environment cannot be represented solely by its associated charges. Some charge transfer (charge neutralization) is expected. As an extreme example of this, we suppose that the positive environment about the  $\text{BH}_3^-$  ion induces an orbital exponent and bond length similar to  $\text{CH}_3$  ( $\alpha = 1.4$ ,  $R(\text{B}-\text{H}) = 2$  a.u.). The results are in table 2. The similarity of these results to those obtained by placing an extra positive charge on the boron nucleus is noted, and the proton coupling constants are now in better agreement with experiment.

TABLE 4.—THEORETICAL RESULTS (AFTER QUARTET SPIN STATE ANNIHILATION) FOR  $\text{BH}_3^-$  WITH AN ENVIRONMENT OF SIX LITHIUM IONS (UNIT CELL 8.22 a.u.) REPRESENTED BY (i) SIX POSITIVE CHARGES; (ii) SIX POSITIVE CHARGES WITH LITHIUM 2s ATOMIC ORBITALS

environment	angle of bending	total energy (a.u.)	hyperfine coupling constants $a(^{11}\text{B})$	$a(^1\text{H})$
(i)	0°	-25.635 15	22.25	-19.97
(i)	2°	-25.635 18	23.53	-19.75
(i)	5°	-25.635 31	30.04	-18.68
(i)	8°	-25.635 43	41.21	-16.92
(i)	10°	-25.635 38	50.62	-15.53
(ii)	0°	-25.641 86	19.90	-17.72
(ii)	2°	-25.641 88	21.01	-17.52
(ii)	5°	-25.641 94	26.68	-16.58
(ii)	8°	-25.641 93	36.49	-14.98
(ii)	10°	-25.641 77	44.84	-13.69

Although  $\text{BH}_3^-$  has not been observed in  $\text{LiBH}_4$  it is more convenient computationally to use an environment of  $\text{Li}^+$  ions instead of  $\text{Na}^+$  ions (unit cell size 8.22 a.u.). It was shown that six lithium ions (using only 1s orbitals on the lithium nuclei) occupying nearest neighbour lattice positions had a minimal effect on the free radical ion coupling constants, i.e. the lithium ions behaved like unit positive charges. It seemed logical to absorb the 1s electrons into the lithium nucleus but include the



unoccupied 2s lithium orbitals in the calculation (expressed as linear combinations of 3 Gaussian functions<sup>33</sup>). The results are given in table 4, together with those where the Li<sup>+</sup> ion is represented by a unit positive charge. The six positive charge environment slightly reduces the angle of bending to about 8°, whereas this is reduced to about 6° using the lithium 2s atomic orbital on each environment centre. The boron hyperfine coupling constants are reduced in the simulated lithium environment but, more important, the barrier height between the two bent configurations in now only 0.000 08 a.u. compared to 0.0003 a.u. for the isolated system. However, although the trend is in all cases towards the experimental results the actual changes are relatively small in magnitude. It would seem, if this radical does indeed exist, that the environment interacts with it much more strongly than our lattice models have suggested.

### CONCLUSIONS

The interpretation of the e.s.r. spectra of BH<sub>3</sub><sup>-</sup>, CH<sub>3</sub> and NH<sub>3</sub><sup>+</sup> is complicated by the out-of-plane zero-point energy vibration which obscures the electronic interpretation. There is considerable evidence that, in addition, the properties of BH<sub>3</sub><sup>-</sup> are seriously affected by the environment. In particular, the stable geometry of BH<sub>3</sub><sup>-</sup> is calculated to be bent when isolated but it could be planar if the positively charged environment affects the radical in the manner suggested.

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