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MINDO/3 Study of First-row Triatomic Hydrides HMH, and of their Cations and Anions

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MINDO/3 has been used to calculate the variation of $\Delta H_f^{\ominus}$ and d(M–H) as a function of angle <HMH for eighteen first-row triatomic hydride species, neutral and singly charged. Orbital energies, vertical and adiabatic ionisation energies, and dipole moments for neutral fragments, are also reported.

Introduction

The rationalisation of the structures of small molecules was first attempted in molecular orbital terms by Walsh [1]: the diagrams presented by Walsh have subsequently been supported by the extended-Hückel calculations of Gimarc [2] for the series of neutral molecules NH_n (n = 2, 3, 4). A number of *ab initio* calculations have been made on individual species [*e.g.* 3–5], but where several studies have been made of a single species the agreement has often been less than impressive: for a number of studies have been made of the $^3B_1$ state of CH_2, and the calculated energy minimum varies from <HCH of 100.5° to <HCH of 140° [6].

In this paper, we present the results of MINDO/3 calculations on first-row triatomic hydrides HMH and their cations and anions, having between four and ten valence-shell electrons, as M varies from boron to fluorine. These not only complement the qualitative models of Walsh and Gimarc [1, 2] by rendering them quantitative, but also yield data on equilibrium bonds lengths, heats of formation, ionisation energies, and dipole moments.

Method

All calculations were performed on the University of St. Andrews IBM 360 computer, using the IBM version of MINDO/3 [7, 8]. For each triatomic, a series of eight calculations was performed, with the angle <HMH at fixed values, varying in steps of 15° from 180° to 75°: in each calculation, the bond distances were optimised. In addition, a further calculation was made for each species, simultaneously optimising both the distance M–H and the angle <HMH to find the equilibrium configuration: convergence was often difficult to achieve for <HMH of 75°. For the six-electron species BH_2^-, CH_2, and NH_2^+ both singlet and triplet configurations were investigated.

Results and Discussion

Orbital Energies

In the linear configuration, all species except the $^1A_1$ states of BH_2^-, CH_2, and NH_2^+, and the boron species BH_2^+ and BH_2 were found to adopt the order of molecular orbitals:

$$(1\sigma_g^+)(1\sigma_u^+)(1\pi_u)(2\sigma_g^+)(2\sigma_u^+)$$

The boron species BH_2^+ and BH_2 adopted the order:

$$(1\sigma_g^+)(1\sigma_u^+)(2\sigma_g^+)(1\pi_u)(2\sigma_u^+)$$

On reduction of the angle <HMH from 180°, each of these order gives rise, by descent of symmetry, to the order:

$$(1a_1)(1b_2)(2a_1)(1b_1)(3a_1)(2b_2)$$

since the degeneracy of π_u is broken on bending to $a_1 + b_1$. For most species, the above orbital ordering for the non-linear molecule is maintained for all values of <HMH between 180° and 75°: at low values of <HMH the orbitals $2b_2$ and $3a_1$ cross in CH_2^+ and NH_2^+ ($^1A_1$); the orbitals $2a_1$ and $1b_2$ cross at low values of <HMH only in H_2F^+, H_2F, and H_2O^-.

The orbital energies of a typical example, H_2O, are illustrated in Fig. 1: energies, at 15° increments in the angle <HMH and at the energy minimum, are listed, along with $\Delta H_f^{\ominus}$ and d(M–H) for all eighteen species studied, in Table I.

Heats of Formation

Heats of formation are listed in Table I, as a function of <HMH; the variation of $\Delta H_f^{\ominus}$ with <HMH is shown in Fig. 2–4 for neutral molecules,

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TABLE I. Variation of Orbital Energies, $\Delta H_f^\ominus$, and d(M–H) with Angle <HMH.

<HMH/°	Orbital energy/eV						$\Delta H_f^\ominus$/kcal mol^{-1}	d(M–H)/Å
	$1a_1$	$1b_2$	$2a_1$	$1b_1$	$3a_1$	$2b_2$		
(a) *Four-electron species*								
BH_2^+								
180	−25.329	−19.878	−8.673	−8.427	−8.427	−5.149	271.638	1.1849
165	−25.334	−19.849	−8.977	−8.427	−8.130	−5.178	272.926	1.1855
150	−25.350	−19.760	−9.378	−8.430	−7.754	−5.264	276.815	1.1873
135	−25.376	−19.609	−9.780	−8.435	−7.396	−5.403	283.398	1.1906
120	−25.412	−19.388	−10.178	−8.443	−7.074	−5.588	292.872	1.1956
105	−25.460	−19.086	−10.573	−8.456	−6.802	−5.806	305.618	1.2028
90	−25.527	−18.688	−10.974	−8.480	−6.603	−6.040	322.327	1.2123
75	−25.646	−18.172	−11.410	−8.528	−6.511	−6.262	344.177	1.2228
180	−25.329	−19.878	−8.673	−8.427	−8.427	−5.149	271.638	1.1849
(b) *Five-electron species*								
BH_2								
180	−16.935	−12.069	−4.420	−0.306	−0.306	2.625	70.359	1.2257
165	−16.933	−12.027	−4.559	−0.409	−0.055	2.631	65.121	1.2075
150	−16.970	−11.925	−4.883	−0.469	0.323	2.575	59.479	1.1975
135	−17.007	−11.743	−5.244	−0.492	0.683	2.463	56.643	1.1975
120	−17.063	−11.482	−5.601	−0.508	1.015	2.320	56.832	1.1976
105	−17.144	−11.129	−5.953	−0.526	1.297	2.160	60.375	1.1976
90	−17.242	−10.659	−6.314	−0.550	1.497	1.997	67.694	1.2018
75	−17.403	−10.055	−6.710	−0.593	1.577	1.876	79.234	1.2063
130.156	−17.019	−11.667	−5.361	−0.498	0.793	2.417	56.365	1.1975
CH_2^+								
180	−32.986	−23.172	−13.152	−9.162	−6.982	−3.763	320.578	1.0855
165	−33.013	−23.133	−13.300	−9.171	−6.891	−3.849	318.785	1.0887
150	−33.123	−23.035	−13.696	−9.200	−6.599	−4.040	315.893	1.0905
135	−33.224	−22.816	−14.200	−9.225	−6.210	−4.296	315.009	1.0934
120	−33.316	−22.470	−14.728	−9.244	−5.812	−4.600	317.694	1.0969
105	−33.408	−21.995	−15.252	−9.257	−5.464	−4.941	324.856	1.1014
90	−33.458	−21.360	−15.759	−9.257	−5.228	−5.310	337.223	1.1114
75	−33.542	−20.589	−16.261	−9.247	−5.124	−5.644	355.573	1.1214
136.845	−33.146	−22.807	−14.130	−9.213	−6.287	−4.284	314.994	1.0928
(c) *Six-electron species*								
BH_2^- ($^3B_1$)								
180	−8.624	−4.340	3.444	3.444	8.031	10.473	48.835	1.1322
165	−8.552	−4.281	3.404	3.601	7.961	10.390	44.108	1.1609
150	−8.573	−4.160	3.101	3.751	8.220	10.326	38.121	1.1729
135	−8.638	−3.980	2.747	3.786	8.568	10.225	35.042	1.1757[a]
120	−8.686	−3.723	2.380	3.803	8.854	10.055	34.767	1.1829
105	−8.794	−3.374	2.039	3.795	9.121	9.901	37.594	1.1865[a]
90	−8.920	−2.919	1.687	3.776	9.286	9.731	43.799	1.1895
75	−9.158	−2.331	1.324	3.727	9.336	9.640	53.464	1.1895
128.144	−8.659	−3.873	2.580	3.796	8.705	10.153	34.547	1.1770

TABLE I. *(continued)*

CH_2 ($^3B_1$)								
180	−23.492	−14.262	−3.787	−3.787	2.300	5.439	100.136	1.0641
165	−23.504	−14.217	−3.927	−3.790	2.362	5.344	97.634	1.0688
150	−23.568	−14.090	−4.317	−3.806	2.615	5.130	93.479	1.0753
135	−23.604	−13.831	−4.831	−3.821	2.961	4.837	91.584	1.0853
120	−23.739	−13.490	−5.359	−3.841	3.398	4.557	93.320	1.0853
105	−23.789	−12.979	−5.888	−3.854	3.722	4.185	99.740	1.0953
90	−23.860	−12.335	−6.398	−3.863	3.964	3.806	111.468	1.1053
75	−24.079	−11.570	−6.882	−3.867	4.148	3.515	129.217	1.1053
135.801	−23.668	−13.879	−4.796	−3.825	2.991	4.894	91.545	1.0781
NH_2^+ ($^3B_1$)[b]								
180	−34.092	−26.208	−15.397	−15.397	−6.898	−3.314	262.704	0.9953
165	−34.103	−26.160	−15.515	−15.420	−6.822	−3.407	261.558	0.9974
150	−34.190	−26.032	−15.855	−15.487	−6.576	−3.644	259.550	0.9994
135	−34.218	−25.738	−16.326	−15.543	−6.260	−4.008	259.264	1.0075
120	−34.408	−25.381	−16.877	−15.606	−5.849	−4.400	262.361	1.0075
105	−34.456	−24.805	−17.424	−15.622	−5.535	−4.876	270.106	1.0175
90	−34.540	−24.096	−17.954	−15.613	−5.355	−5.307	283.078	1.0275
140.573	−34.279	−25.902	−16.149	−15.536	−6.354	−3.844	259.011	1.0000
BH_2^- ($^1A_1$)								
180	−8.860	−4.569	−0.547	7.229	7.229	9.660	63.574	1.3612
165	−8.689	−4.426	−0.613	7.308	7.559	9.812	57.832	1.3388
150	−8.588	−4.211	−0.752	7.368	8.017	9.937	48.040	1.3107
135	−8.573	−3.950	−0.958	7.390	8.443	9.958	39.108	1.2922
120	−8.599	−3.620	−1.202	7.398	8.822	9.906	32.686	1.2819
105	−8.648	−3.195	−1.464	7.400	9.145	9.820	29.508	1.2768
90	−8.724	−2.648	−1.739	7.401	9.393	9.741	29.953	1.2739
75	−8.858	−2.050	−1.947	7.401	9.529	9.733	33.992	1.2710
99.241	−8.672	−3.001	−1.568	7.400	9.250	9.785	29.239	1.2757
CH_2 ($^1A_1$)								
180	−23.492	−14.262	−7.777	0.203	2.300	5.439	143.029	1.0641
165	−23.507	−14.207	−7.847	0.211	2.273	5.319	138.883	1.0722
150	−23.561	−14.065	−8.183	0.193	2.301	4.968	127.635	1.0937
135	−23.664	−13.831	−8.732	0.145	2.595	4.608	114.777	1.1082
120	−23.777	−13.462	−9.276	0.115	2.997	4.293	105.173	1.1150
105	−23.888	−12.944	−9.787	0.100	3.375	3.981	100.538	1.1203
90	−23.992	−12.265	−10.270	0.098	3.666	3.674	101.638	1.1269
75	−24.084	−11.406	−10.741	0.114	3.404	3.815	109.002	1.1369
100.177	−23.922	−12.745	−9.945	0.098	3.481	3.881	100.239	1.1222
NH_2^+ ($^1A_1$)								
180	−34.092	−26.208	−20.147	−10.647	−6.898	−3.314	310.901	0.9953
165	−34.103	−26.147	−20.196	−10.668	−6.873	−3.413	308.969	0.9986
150	−34.137	−25.973	−20.368	−10.732	−6.782	−3.695	303.775	1.0075
135	−34.202	−25.694	−20.692	−10.830	−6.599	−4.114	297.171	1.0188
120	−34.303	−25.301	−21.129	−10.929	−6.341	−4.597	291.773	1.0295
105	−34.425	−24.772	−21.606	−11.002	−6.077	−5.095	289.848	1.0393
90	−34.543	−24.090	−22.073	−11.034	−5.889	−5.575	292.782	1.0501
75	−34.618	−23.243	−22.513	−11.010	−5.860	−5.997	301.200	1.0654
106.016	−34.416	−24.813	−21.574	−10.998	−6.093	−5.061	289.836	1.0386

TABLE I. *(continued)*

(d) *Seven-electron species*								
CH_2^-								
180	−13.887	−5.234	1.624	5.614	11.639	14.662	146.180	1.0526
165	−13.891	−5.186	1.575	5.627	11.553	14.524	142.295	1.0626
150	−13.876	−5.079	1.204	5.594	11.278	13.982	130.566	1.1024
135	−13.931	−4.866	0.533	5.505	11.463	13.493	116.243	1.1291
120	−14.027	−4.485	−0.022	5.474	11.886	13.187	105.918	1.1366
105	−14.127	−3.953	−0.522	5.461	12.286	12.888	100.951	1.1420
90	−14.227	−3.257	−0.992	5.457	12.585	12.598	101.970	1.1487
75	−14.324	−2.377	−1.452	5.464	12.306	12.773	109.600	1.1590
99.891	−14.162	−3.735	−0.685	5.459	12.405	12.785	100.597	1.1440
NH_2								
180	−24.119	−16.192	−9.262	−4.516	3.148	7.004	61.022	0.9690
165	−24.120	−16.133	−9.309	−4.542	3.141	6.883	58.531	0.9737
150	−24.116	−15.962	−9.497	−4.637	3.145	6.522	51.563	0.9876
135	−24.122	−15.686	−9.908	−4.789	3.253	5.986	42.186	1.0063
120	−24.180	−15.282	−10.463	−4.932	3.513	5.424	34.050	1.0219
105	−24.284	−14.721	−11.032	−5.029	3.824	4.891	30.181	1.0339
90	−24.401	−13.991	−11.569	−5.078	4.076	4.388	32.175	1.0455
75	−24.495	−13.081	−12.071	−5.078	3.930	4.182	40.870	1.0605
102.214	−24.306	−14.599	−11.135	−5.041	3.878	4.795	30.077	1.0360
H_2O^+								
180	−39.900	−29.605	−24.118	−18.783	−7.724	−3.209	250.203	0.9487
165	−39.932	−29.556	−24.203	−18.814	−7.679	−3.324	248.320	0.9509
150	−40.026	−29.412	−24.462	−18.898	−7.541	−3.648	243.358	0.9562
135	−40.170	−29.168	−24.877	−19.016	−7.319	−4.121	237.383	0.9628
120	−40.338	−28.806	−25.394	−19.131	−7.054	−4.677	232.808	0.9692
105	−40.499	−28.305	−25.948	−19.214	−6.818	−5.267	231.664	0.9761
90	−40.619	−27.655	−26.493	−19.246	−6.690	−5.849	235.245	0.9851
75	−40.649	−27.005	−26.858	−19.210	−6.759	−6.375	244.250	0.9994
108.419	−40.464	−28.432	−25.821	−19.199	−6.865	−5.132	231.544	0.9745
(e) *Eight-electron species*								
NH_2^-								
180	−13.887	−6.041	1.700	1.700	13.192	17.383	103.325	0.9584
165	−13.872	−5.995	1.655	1.654	13.116	17.217	100.009	0.9658
150	−13.770	−5.887	1.388	1.455	12.849	16.620	89.965	0.9938
135	−13.622	−5.712	0.627	1.096	12.711	15.708	75.324	1.0339
120	−13.678	−5.322	−0.121	0.908	13.050	15.100	63.191	1.0520
105	−13.781	−4.735	−0.759	0.818	13.465	14.604	57.001	1.0623
90	−13.905	−3.964	−1.334	0.771	13.804	14.128	57.788	1.0727
75	−14.009	−3.002	−1.877	0.756	13.667	13.991	66.289	1.0870
99.057	−13.831	−4.451	−0.993	0.796	13.613	14.414	56.438	1.0662
H_2O								
180	−29.163	−18.816	−12.235	−12.235	3.081	7.955	−24.348	0.9002
165	−29.179	−18.756	−12.316	−12.268	3.097	7.812	−26.958	0.9039
150	−29.231	−18.584	−12.585	−12.367	3.169	7.406	−33.959	0.9139
135	−29.324	−18.301	−13.058	−12.512	3.347	6.822	−42.870	0.9265

TABLE I. *(continued)*

120	−29.454	−17.886	−13.667	−12.655	3.624	6.171	−50.342	0.9379
105	−29.594	−17.316	−14.313	−12.758	3.917	5.514	−53.591	0.9480
90	−29.712	−16.578	−14.943	−12.807	4.130	4.875	−50.909	0.9587
75	−29.760	−15.676	−15.537	−12.789	4.166	4.278	−41.256	0.9736
104.027	−29.610	−17.276	−14.355	−12.764	3.940	5.476	−53.610	0.9481
H_2F^+								
180	−48.401	−27.755	−25.007	−25.007	−9.595	−4.952	167.076	0.9461
165	−48.504	−27.802	−25.151	−25.099	−9.560	−5.081	165.533	0.9474
150	−48.758	−27.898	−25.530	−25.324	−9.467	−5.414	161.721	0.9502
135	−49.064	−27.965	−26.048	−25.593	−9.349	−5.854	157.392	0.9529
120	−49.359	−27.954	−26.630	−25.846	−9.251	−6.334	154.186	0.9550
105	−49.620	−27.852	−27.242	−26.062	−9.221	−6.805	153.184	0.9570
90	−49.839	−27.666	−27.873	−26.237	−9.306	−7.224	154.892	0.9602
75	−50.009	−27.416	−28.529	−26.372	−9.552	−7.529	159.524	0.9682
106.713	−49.592	−27.868	−27.171	−26.040	−9.219	−6.753	153.167	0.9568
(f) *Nine-electron species*								
H_2O^-								
180	−17.277	−8.420	−1.853	−1.853	6.162	15.829	26.885	1.0231
165	−17.329	−8.392	−2.057	−1.943	6.242	15.645	24.167	1.0277
150	−17.439	−8.261	−2.587	−2.127	6.509	15.222	18.975	1.0378
135	−17.564	−7.973	−3.248	−2.275	6.965	14.782	15.676	1.0452
120	−17.666	−7.496	−3.915	−2.353	7.487	14.356	16.228	1.0509
105	−17.710	−6.819	−4.549	−2.371	7.952	13.907	20.767	1.0592
90	−17.704	−5.954	−5.124	−2.320	8.317	13.487	29.418	1.0692
75	−17.585	−4.899	−5.649	−2.192	8.465	13.078	40.415	1.0874
133.487	−17.571	−7.931	−3.317	−2.287	7.010	14.731	15.544	1.0464
H_2F[b]								
180	−38.419	−18.148	−14.953	−14.953	−5.065	3.745	−57.995	0.9545
165	−38.483	−18.152	−15.080	−15.005	−4.996	3.676	−58.758	0.9534
150	−38.623	−18.123	−15.408	−15.120	−4.813	3.497	−60.484	0.9519
135	−38.762	−18.000	−15.843	−15.228	−4.566	3.273	−62.107	0.9500
120	−38.851	−17.748	−16.315	−15.288	−4.309	3.048	−62.944	0.9489
105	−38.877	−17.364	−16.793	−15.284	−4.091	2.867	−63.004	0.9482
90	−38.836	−16.861	−17.272	−15.210	−3.963	2.777	−62.931	0.9483
112.880	−38.873	−17.582	−16.542	−15.295	−4.197	2.955	−63.042	0.9484
(g) *Ten-electron species*								
H_2F^-								
180	−28.663	−8.863	−5.249	−5.249	−0.703	12.117	−68.386	0.9998
165	−28.642	−8.788	−5.329	−5.229	−0.606	12.110	−66.820	0.9997
150	−28.578	−8.563	−5.543	−5.164	−0.340	12.093	−62.263	0.9992
135	−28.464	−8.183	−5.834	−5.048	0.035	12.081	−55.166	0.9984
120	−28.284	−7.643	−6.147	−4.866	0.458	12.100	−46.363	0.9972
105	−28.021	−6.939	−6.447	−4.602	0.874	12.183	−37.172	0.9963
90	−27.652	−6.726	−6.074	−4.237	1.227	12.363	−29.481	0.9976
75	−27.155	−7.023	−5.079	−3.769	1.452	12.461	−25.514	1.0070
180	−28.663	−8.863	−5.249	−5.249	−0.703	12.117	−68.386	0.9998

[a] Interpolation. [b] Fails to converge when <HMH = 75°.

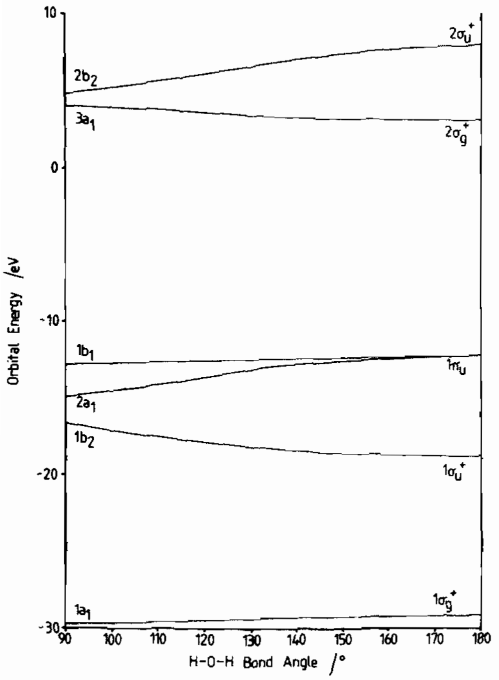

Fig. 1. Orbital energies as a function of H–O–H angle in H_2O.

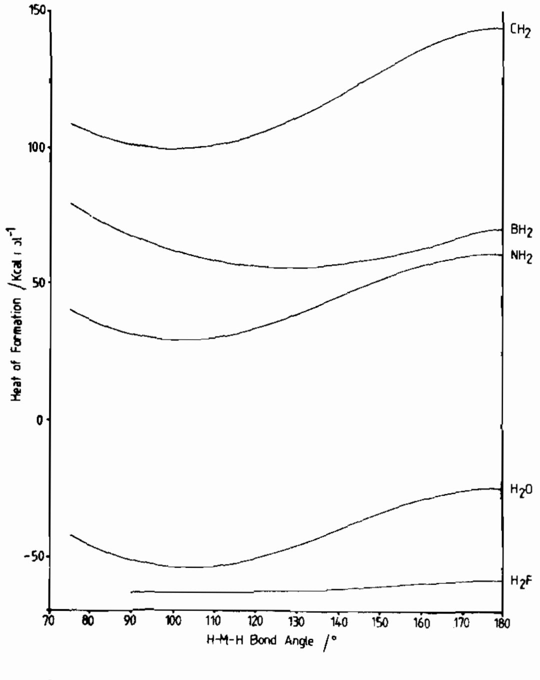

Fig. 2. Heat of formation of neutral MH_2 as a function of H–M–H angle.

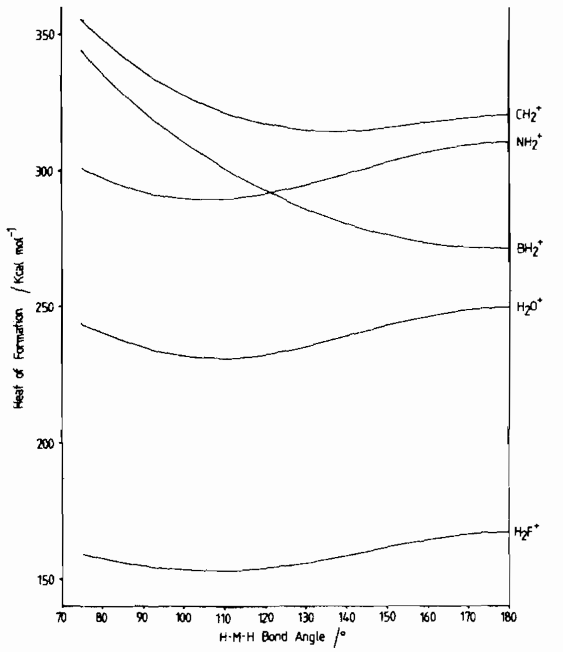

Fig. 3. Heat of formation of cationic $(MH_2)^+$ as a function of H–M–H angle.

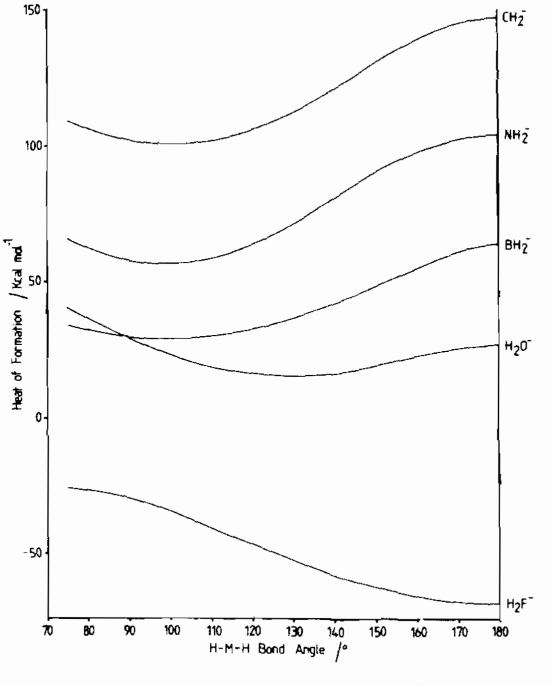

Fig. 4. Heat of formation of anionic $(MH_2)^-$ as a function of H–M–H angle.

cations and anions respectively. Equilibrium values for BH_2, CH_2 ($^3B_1$), NH_2 and H_2O are computed to be, respectively, (kcal mol^{-1}): +56.37, +91.55, +30.08, and −53.61. These may be compared with the experimental values (kcal mol^{-1}): +48, +95(±5), +40.3, and −57.80 [9].

TABLE II. Molecular Properties at Equilibrium.

(a) *Neutral molecules*

Number of electrons	Formula	State	<HMH/°	d/(M–H)/Å	$\Delta H_f^\ominus$/kcal mol^{-1}	Electron Population		Dipole Moment/D
						M	H	
5	BH_2	$^2A_1$	130.16	1.1984	+56.37	2.820	1.090	0.321
6	CH_2	$^1A_1$	100.18	1.1222	+100.24	3.812	1.094	1.043
6	CH_2	$^3B_1$	135.80	1.0781	+91.55	4.146	0.927	0.896
7	NH_2	$^2B_1$	102.21	1.0360	+30.08	5.092	0.954	1.457
8	H_2O	$^1A_1$	104.03	0.9481	−53.61	6.506	0.747	2.108
9	H_2F	$^2A_1$	112.88	0.9484	−63.04	7.220	0.890	0.716

(b) *Cations*

Number of electrons	Formula	State	<HMH/°	d(M–H)/Å	$\Delta H_f^\ominus$/kcal mol^{-1}	Electron Population	
						M	H
4	BH_2^+	$^1\Sigma_g^+$	180.00	1.1849	+271.64	2.280	0.860
5	CH_2^+	$^2A_1$	136.85	1.0928	+314.99	3.278	0.861
6	NH_2^+	$^1A_1$	106.02	1.0386	+289.84	4.368	0.816
6	NH_2^+	$^3B_1$	140.57	1.0000	+259.01	4.504	0.748
7	H_2O^+	$^2B_1$	108.42	0.9745	+231.54	5.798	0.604
8	H_2F^+	$^1A_1$	106.71	0.9568	+153.17	7.132	0.434

(c) *Anions*

Number of electrons	Formula	State	<HMH/°	d(M–H)/Å	$\Delta H_f^\ominus$/kcal mol^{-1}	Electron Population	
						M	H
6	BH_2^-	$^1A_1$	99.24	1.2757	+29.24	3.394	1.303
6	BH_2^-	$^3B_1$	128.14	1.1770	+34.55	3.942	1.029
7	CH_2^-	$^2B_1$	99.89	1.1440	+100.60	4.628	1.186
8	NH_2^-	$^1A_1$	99.06	1.0662	+56.44	5.768	1.116
9	H_2O^-	$^2A_1$	133.49	1.0464	+15.54	6.726	1.137
10	H_2F^-	$^1\Sigma_g^+$	180.00	0.9998	−68.39	7.176	1.412

TABLE III. H...H Distances at Equilibrium.

MH_2^+	d(H...H)/Å	<HMH/°	MH_2	d(H...H)/Å	<HMH/°	MH_2^-	d(H...H)/Å	<HMH/°
BH_2^+	2.3698	180.00	–	–	–	–	–	–
CH_2^+	2.0324	136.85	BH_2	2.1736	130.16	–	–	–
$NH_2^+(^1A_1)$	1.6591	106.02	$CH_2(^1A_1)$	1.7215	100.18	$BH_2^-(^1A_1)$	1.9436	99.24
$NH_2^+(^3B_1)$	1.8828	140.57	$CH_2(^3B_1)$	1.9978	135.80	$BH_2^-(^3B_1)$	2.1170	128.14
H_2O^+	1.5809	108.42	NH_2	1.6127	102.21	CH_2^-	1.7513	99.89
H_2F^+	1.5354	106.71	H_2O	1.4945	104.03	NH_2^-	1.6222	99.06
–	–	–	H_2F	1.5806	112.88	H_2O^-	1.9228	133.49
–	–	–	–	–	–	H_2F^-	1.9996	180.00

Molecular Structures at Equilibrium

Table II records the values of <HMH and d(M–H) corresponding to the minimum energy. For comparison, some experimental values are: BH_2, <HBH 131°, d(B–H) 1.18 Å [10]; $CH_2(^1A_1)$, <HCH 102.4°, d(C–H) 1.111 Å [11]; $CH_2(^3B_1)$, <HCH 136 ± 8°,

d(C–H) 1.078 Å [12, 13]; NH_2, $\angle$HNH 103.4°, d(N–H) 1.024 Å [10]; H_2O, $\angle$HOH 104.53°, d(H–O) 0.9571 [14]: in general, the agreement is excellent. *Ab initio* computations, but no experimental results, have been reported for NH_2^+ [3], H_2O^+ [4], and H_2F^+ [5]; the angles predicted at the energy minima are: NH_2^+ ($^3B_1$), ~140° [3]; NH_2^+ ($^1A_1$), ~120° [3]; H_2O^+, 112.5° [4]; H_2F^+, 116° [5].

In Table III are listed the formally non-bonded distances d(H...H) corresponding to the equilibrium geometries: at small angles $\angle$HMH, the minimal values of d(H...H), in BH_2^- ($^1A_1$), CH_2 ($^1A_1$), NH_2, H_2O and H_2F^+, correspond to computed effective non-bonded radii for hydrogen atoms as follows: H_B, 0.97 Å, H_C, 0.86 Å; H_N, 0.81 Å; H_O, 0.75 Å; H_F, 0.77 Å. The corresponding experimental values are: H_B, 1.07 Å; H_C, 0.87 Å; H_N, 0.80 Å; H_O,, 0.76 Å.

The geometrical data in Tables II and III give full support to the generalisations of Walsh [1] and Gimarc [2], namely that species HMH having either four or ten valence-shell electrons will have linear ground states, and that those having between five and nine will have non-linear ground states, with generally wider angles for five and nine electrons, and values closer to 100° for six, seven, and eight electrons. Similarly, on ionisation, the removal of an entirely non bonding electron from $1b_1$ occasions very little geometrical change, as in the ionisations:

$H_2O \rightarrow H_2O^+$
$NH_2^- \rightarrow NH_2 \rightarrow NH_2^+ (^1A_1)$
$CH_2^- \rightarrow CH_2 (^1A_1)$
$CH_2 (^3B_1) \rightarrow CH_2^+$
$BH_2^- (^3B_1) \rightarrow BH_2$

Six-electron Species

There has been immense interest shown, both experimentally [11–13] and theoretically [6, 15] in the six-electron fragment CH_2, but rather little in the analogous BH_2^- and NH_2^+. MINDO/3 calculations have been reported previously [15] for CH_2, and our own results concur. In each of the triplets the orbital ordering is, for $\angle$HMH of 180°:

$$(1\sigma_g^+)(1\sigma_u^+)(1\pi_u)(2\sigma_g^+)(2\sigma_u^+)$$

in which the two components of $1\pi_u$ are each singly occupied, and of identical energy (*cf.* Table I): when the singlets CH_2 and NH_2^+ are constrained to be linear, with double occupation of one component of $1\pi_u$, the occupied orbital is substantially tighter bound than the unoccupied, but the mean of the two energies is exactly that in the corresponding triplet. The energies of the four remaining orbitals $1\sigma_g^+$, $1\sigma_u^+$, $2\sigma_g^+$, and $2\sigma_u^+$ are identical in CH_2 ($^1A_1$) and CH_2 ($^3B_1$), and in NH_2^+ ($^1A_1$) and NH_2^+ ($^3B_1$). In the linear configuration of BH_2^- ($^1A_1$) the orbital ordering is

$$(1\sigma_g^+)(1\sigma_u^+)(2\sigma_g^+)(1\pi_u)(2\sigma_u^+)$$

which readily accommodates a singlet configuration. BH_2^- ($^3B_1$) is the only boron species studied here for which $1\pi_u$ is calculated to be tighter bound than $2\sigma_g^+$.

In CH_2 and NH_2^+, the triplets are calculated to be the more stable by 8.69 and 30.83 kcal mol^{-1} respectively, whereas in BH_2^- the singlet is calculated to be the more stable by 5.31 kcal mol^{-1}: the variations of $\Delta H_f^\ominus$ with $\angle$HMH for singlets and triplets of BH_2^-, CH_2, and NH_2^+ are shown in Fig. 5.

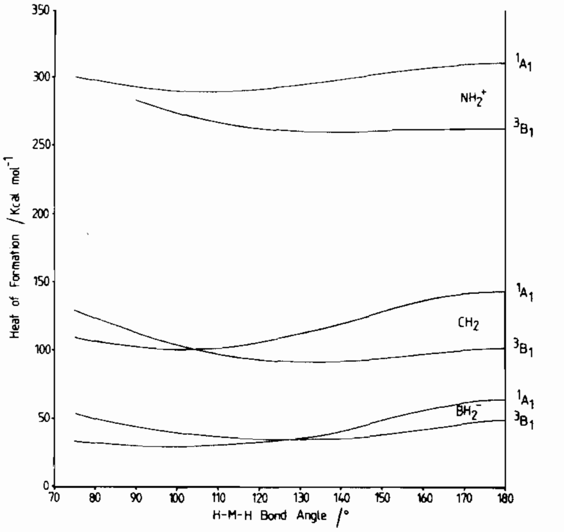

Fig. 5. Heat of formation of singlet and triplet NH_2^+, CH_2 and BH_2^- as a function of H–M–H angle.

Ionisation Energies

The valence-shell vertical ionisation energies calculated for neutral H_2O are (eV): 12.76, 14.36, 17.28, and 29.61, the first three of which correspond well with those observed in the He–I photoelectron spectrum [16]: 12.61 eV, 13.89 eV, and 17.20 eV. In Table IV are listed calculated values of the first ionisation energies: vertical ionisation energies are calculated, using Koopmann's theorem, from the binding energies of the HOMO; adiabatic ionisation energies are calculated from the total energies of the parent and its ionised daughter, both at equilibrium. The adiabatic energies correspond reasonably well with the few experimental data available [17], thus: BH_2, 8.12 eV; CH_2 ($^3B_1$), 11.82 eV; NH_2, 11.4 eV (probably ionisation to ($^1A_1$)NH_2^+); and H_2O, 12.61 eV. It is noteworthy that while in diamagnetic species, the adiabatic ionisation energy is always calculated to be slightly lower than the vertical ionisation energy, as expected, even in unbound species such as NH_2^- and feebly bound species such as H_2F^-, in paramagnetic species, the vertical ionisation energy is invariably seriously underestimated: if this is a

TABLE IV. First Ionisation Energies/eV.

	Vertical	Adiabatic
BH_2^+	19.88	–
BH_2	5.36	9.34
BH_2^- ($^1A_1$)	1.57	1.18
BH_2^- ($^3B_1$)	–3.80	0.95
CH_2^+	14.13	–
CH_2 ($^1A_1$)	9.95	9.31
CH_2 ($^3B_1$)	3.83	9.69
CH_2^-	–5.46	–0.39[a], –0.02[b]
NH_2^+ ($^1A_1$)	21.57	–
NH_2^+ ($^3B_1$)	15.54	–
NH_2	5.04	9.93[a], 11.26[b]
NH_2^-	–0.80	–1.14
H_2O^+	19.20	–
H_2O	12.76	12.37
H_2O^-	–7.01	–3.00
H_2F^+	26.04	–
H_2F	4.20	9.28
H_2F^-	0.70	0.23

[a] Ionisation to ($^3B_1$) MH_2^+. [b] Ionisation to ($^1A_1$) MH_2^+.

systematic error in MINDO/3, it is readily recognised by comparison of vertical and adiabatic ionisation energies.

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