Ab initio and Semiempirical Studies on $H_3C-B=O$ and $H-B=O$. Their Structure and Vibrational Spectra

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Z. Naturforsch. **42a**, 1027–1036 (1987); received June 6, 1987

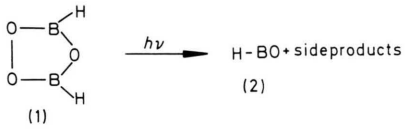
The electronic structure of H_3C-BO and $H-BO$ is elucidated employing one determinant *ab initio* calculations with STO-3G and 4-31G basis sets and the semiempirical MNDO theory. The vibrational spectra of both molecules including various isotopic shifts have been calculated at the 4-31G level. The influence of methyl substitution on the vibrational frequencies, BO stretching force constant, Mulliken charges, and vertical ionization potential is examined and compared with that in the pairs $H-CN/H_3C-CN$ and $H-NC/H_3C-NC$, isoelectronic with $H-BO/H_3C-BO$.

As judged from a comparison of the force constants for stretching the XY bonds in the H_3C-XY and $H-XY$ molecules, the XY bond is "softened" upon methyl substitution. This effect is found to decrease in the order $H_3C-BO > H_3C-CN > H_3C-NC$.

For XY=BO the difference between the first ionization potentials of $H-XY$ and H_3C-XY is found to be somewhat smaller than for XY = CN but slightly higher than for the isonitril compounds (XY = NC).

Introduction

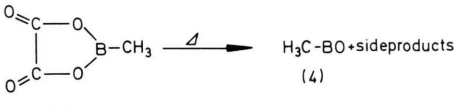
Some years ago Lory and Porter [1] published the results of matrix isolation experiments, in which a mixture of **(1)** [a] and argon, deposited on a CsJ target window at 5 K, was irradiated at 148 and 184.9 nm. Photolysis of the precursor led to oxoborane (H – BO) **(2)**, which was identified by means of its IR spectrum.



(1) (2)

Recently H-BO was detected in the gas phase after electric discharge in B_2H_6/O_2 and B_2H_6/NO mixtures [9]. In these experiments it was possible to determine rotational constants of $H-{}^{11}BO$.

Although H – BO has been subjected to the scrutiny of experimental [1, 9, 10] and theoretical studies [11–16, 17, 18, 19], only little is known about its methyl derivative methyloxoborane (H_3C-BO) **(4)** [20, 21]. The results of some trapping experiments suggest that methyloxoborane is formed during the thermal decomposition of **(3)**, because thermolysis of **(3)** and subsequent intrusion of the pyrolysis gas into a solution containing an 1,3-dipole yielded a compound which might be the trapping product of **(4)** [20].



(3) (4)

At the moment, extensive work on the photoelectron spectrum of H_3C-BO is in progress in the group of Bock [22].

The only theoretical paper dealing with **(4)** that came to our knowledge was a quantumchemical study about the energetics of sequential 1,2-shifts in organoborates from boron to carbon. In that study H_3C-BO was compared with its isomers H_2B-CHO and $H_3B^- - C^+O$ [21]. Employing the

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STO-3G basis set, $H_3B^- - C^+O$ was found to be 246.2 kJ/mol higher in energy than H_3C-BO. Even less favourable is H_2B-CHO: at the same level of theory it is 340.0 kJ/mol higher in energy than (**4**) [21].

In this paper we present the theoretical vibrational spectra of H – BO and H_3C-BO, calculated at the 4-31G level of *ab initio* theory. In the case of H_3C-BO the spectra were calculated for the two isotopomers containing either ^{10}B or ^{11}B.

To study the influence of the methyl group and to get an idea of the reliability of the theoretical frequencies, we also calculated the vibrational spectra of the molecules $H-{}^{10}BO$, $H-{}^{11}BO$, $D-{}^{10}BO$, and $D-{}^{11}BO$ for which the experimental frequencies are available [1].

The role of the methyl group was further elucidated by calculating vertical ionization potentials and Mulliken total and π charges [23 – 26] for both oxoboranes.

In H – XY four electrons occupy two molecular orbitals of π symmetry. We therefore interpret the difference between four and the Mulliken number of "π electrons" in the isoelectronic XY groups of H_3C-XY as the π charge of this group (XY = BO, CN, and NC).

The results for H_3C-BO and H – BO are compared with those for the pairs H_3C-CN/H – CN and H_3C-NC/H – NC.

Computational Method

The calculations have been performed on the CDC CYBER 175 computer system of the Rechenzentrum der Rheinisch-Westfälischen Technischen Hochschule Aachen. All molecules have been fully optimized at the one determinant *ab initio* level, employing the STO-3G [27] and 4-31G [28] basis sets and the semiempirical MNDO method [29].

The *ab initio* calculations were performed using the HONDO5 program package [30], whereas the standard MNDO program [31] was employed for the semiempirical calculations. All vibrational spectra were obtained with the 4-31G basis set, using numerical differentiation of analytical gradients [32, 33]. Although the basis set used is still rather small, the vibrational spectra obtained at this level are known to coincide qualitatively with their experimental counterparts [34]. However, for numerical reasons the vibrational spectra for H_3C-BO, H_3C-CN, and H_3C-NC have been calculated under constraint of C_{3v} symmetry [35].

To calculate the isotopic shifts, the cartesian force constant matrix prior to massweighting was assumed to be the same for isotopomers [36]. Consequently, only different masses have been used to set up the massweighted force constant matrices for isotopomers.

For hydrogen, carbon, and nitrogen we used the atomic masses 1.00797, 12.01115, and 14.00670, respectively. These are the standard values implemented in the HONDO5 program. It should be kept in mind, however, that these values are mean atomic masses. For the elements mentioned above, the average values are rather close to the masses of the most abundant isotopes, and no considerable error is introduced by using these data. However, if more than one isotope contributes significantly to the natural composition of the element (as for example in the case of boron and chlorine) a separate calculation has to be performed for each isotopomer.

Results and Discussion

The optimized total energies (STO-3G and 4-31G) are listed in Table 1. The corresponding geometries of the molecules under consideration are given in Table 2.

Checking the eigenvalues of the force constant matrices revealed that the C_{3v} structure of H_3C-BO and the linear $C_{\infty v}$ structure of H – BO [b] are true minima at the 4-31G level.

The Mulliken total and π charges are given in Table 3.

The calculated and experimental vibrational frequencies of $H-{}^{10}BO$, $H-{}^{11}BO$, $D-{}^{10}BO$, and $D-{}^{11}BO$ are listed in Table 4. The calculated

Table 1. Total energies of the molecules H – XY and H_3C-XY according to STO-3G and 4-31G (all values in a.u.).

Molecule	STO-3G	4-31G
H – BO	– 98.826900	– 100.018673
H – CN	– 91.675209	– 92.731928
H – NC	– 91.644437	– 92.716779
H_3C-BO	– 137.425791	– 139.026576
H_3C-CN	– 130.271542	– 131.728262
H_3C-NC	– 130.233170	– 131.694201

Table 2. Bond lengths (in pm) and bond angles (in degrees) in H – BO, H_3C – BO, H – CN, H_3C – CN, H – NC and H_3C – NC. For numbering of atoms see Figure 1.

	H – BO [$C_{\infty v}$]		
Parameter	4-31G	STO-3G	MNDO
r(H – B)	115.2	114.2	114.1
r(B – O)	119.9	117.6	117.3
	H_3C – BO [C_{3v}]		
Parameter	4-31G	STO-3G	MNDO
r(C – H)	108.3	108.5	110.9
r(C – B)	152.8	154.6	152.5
r(B – O)	120.4	117.8	117.6
<HCH	108.1	108.2	109.2
<HCB	110.8	110.7	109.7
	H – CN [$C_{\infty v}$]		
Parameter	4-31G	STO-3G	MNDO
r(H – C)	105.2	107.0	105.5
r(C – N)	114.0	115.3	116.0
	H_3C – CN [C_{3v}]		
Parameter	4-31G	STO-3G	MNDO
r(C – H)	108.0	108.8	111.0
$r(C_1 - C_2)$	145.5	148.7	145.2
$r(C_2 - N)$	114.2	115.4	116.2
<HCH	108.4	109.0	108.3
$<HC_1C_2$	110.5	110.0	110.6
	H – NC [$C_{\infty v}$]		
Parameter	4-31G	STO-3G	MNDO
r(H – N)	97.8	101.1	97.5
r(N – C)	116.2	117.0	118.4
	H_3C – NC [C_{3v}]		
Parameter	4-31G	STO-3G	MNDO
r(C – H)	107.9	109.2	111.5
$r(C_1 - N)$	141.9	144.6	142.4
$r(N - C_2)$	116.1	117.1	119.0
<HCH	108.8	109.2	108.7
$<HC_1N$	110.1	109.7	110.2

spectra are represented in Figure 2. The cartesian displacement vectors are shown in Figure 3.

As known from other cases at this level of theory, the calculated vibrational frequencies are higher than the experimental ones [34]. The largest difference between experimental and calculated vibrational frequencies (ca. 14% relative to the experimental value) was found for the bending mode which for H – ^{11}BO (H – ^{10}BO) was observed at 754 cm^{-1} (764 cm^{-1}). The smallest deviation from the measured value (ca. 6% relative to the experimental value) was found for the vibration which is mainly ν(B – O) and which for H – ^{11}BO (H – ^{10}BO) was observed at 1817 cm^{-1} (1855 cm^{-1}). In the gas phase this vibration was observed at 1825.6 cm^{-1} [9] for H – ^{11}BO. With an average difference of somewhat more than 8% the value for the ν(H – B) vibration which appears at 2849 cm^{-1} (2874 cm^{-1}) for H – ^{11}BO (H – ^{10}BO) lies between these two extrema. Similar differences between calculated and observed values were found in the case of the deuterated molecules. By means of the calculated normal modes the vibrations for these molecules can be assigned as follows: For D – ^{11}BO (D – ^{10}BO) the vibration observed at 2259 cm^{-1} (2303 cm^{-1}) is mainly stretching of the DB bond, whereas stretching of the BO bond in D – ^{11}BO (D – ^{10}BO) appears at 1648 cm^{-1} (1663 cm^{-1}). Finally, deformation of the D – B – O bond angle occurs at 606 cm^{-1} (617 cm^{-1}) for D – ^{11}BO (D – ^{10}BO).

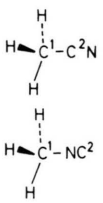

Fig. 1

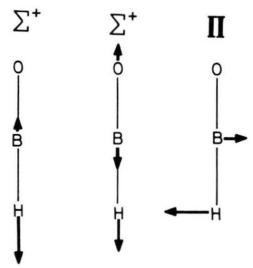

Fig. 3

Fig. 1. Numbering of atoms in H_3C – CN and H_3C – NC.

Fig. 3. Normal modes of H – ^{11}BO. Only one member of the degenerate pair (π) is shown.

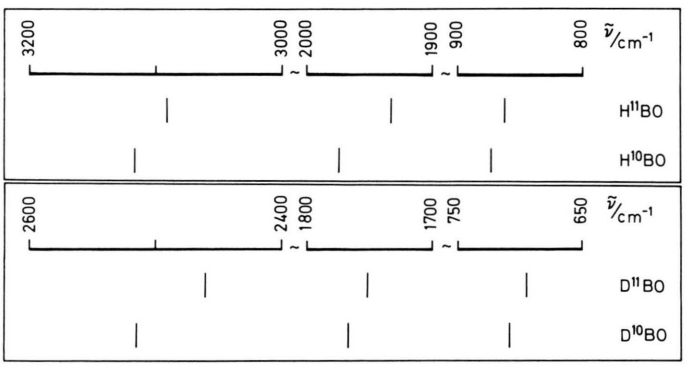

Fig. 2. Schematic representation of the calculated vibrational spectra of H – ^{11}BO, H – ^{10}BO, D – ^{11}BO and D – ^{10}BO.

Table 3. Mulliken charges in H – BO, H_3C – BO, H – CN, H_3C – CN, H – NC and H_3C – NC. For numbering of atoms see Figure 1.

	H – BO [$C_{\infty v}$]		
	4-31G	STO-3G	MNDO
q(H)	0.0655	−0.0077	0.1616
q(B)	0.5284	0.2979	−0.0232
q(O)	−0.5940	−0.2902	−0.1384
q_π(B)	0.1580	−0.1278	−0.0167
q_σ(BO)	−0.0655	0.0077	−0.1616
	H_3C – BO [C_{3v}]		
	4-31G	STO-3G	MNDO
q(H)	0.2120	0.0798	0.0210
q(C)	−0.7732	−0.2927	0.1331
q(B)	0.7289	0.3661	−0.0618
q(O)	−0.5916	−0.3128	−0.1343
q(CH_3)	−0.1373	−0.0534	0.1961
q_π(B)	0.1245	−0.1381	−0.0680
q_π(O)	−0.1802	0.0945	0.0144
q_π(BO)	−0.0557	−0.0436	−0.0536
q_σ(BO)	0.1931	0.0970	−0.1425
	H – CN [$C_{\infty v}$]		
	4-31G	STO-3G	MNDO
q(H)	0.3260	0.1496	0.1900
q(C)	0.0107	0.0117	−0.0891
q(N)	−0.3367	−0.1613	−0.1009
q_π(C)	0.1136	0.0566	0.1426
q_σ(CN)	−0.3260	−0.1496	−0.1900
	H_3C – CN [C_{3v}]		
	4-31G	STO-3G	MNDO
q(H)	0.2207	0.1012	0.0209
q(C_1)	−0.4431	−0.1807	0.1317
q(C_2)	0.1908	0.0750	−0.1138
q(N)	−0.4098	−0.1980	−0.0805
q(CH_3)	0.2190	0.1230	0.1944
q_π(C_2)	0.1179	0.0771	0.1153
q_π(N)	−0.1555	−0.1032	−0.1375
q_π(CN)	−0.0376	−0.0261	−0.0222
q_σ(CN)	−0.1814	−0.0969	−0.1721
	H – NC [$C_{\infty v}$]		
	4-31G	STO-3G	MNDO
q(H)	0.4353	0.2648	0.2556
q(N)	−0.7375	−0.3988	−0.4371
q(C)	0.3022	0.1340	0.1815
q_π(N)	0.0352	0.1705	0.1341
q_σ(NC)	−0.4353	−0.2648	−0.2556
	H_3C – NC [C_{3v}]		
	4-31G	STO-3G	MNDO
q(H)	0.2041	0.0987	0.0006
q(C_1)	−0.1553	−0.0618	0.2700
q(N)	−0.6697	−0.3325	−0.4644
q(C_2)	0.2127	0.0982	0.1926
q(CH_3)	0.4570	0.2343	0.2717
q_π(C_2)	−0.0776	−0.2113	−0.1214
q_π(N)	0.0656	0.2147	0.1334
q_π(NC)	−0.0119	0.0034	0.0120
q_σ(NC)	−0.4452	−0.2377	−0.2837

Table 4. Calculated and experimental vibrational frequencies for H – ^{11}BO, H – ^{10}BO, D – ^{11}BO, and D – ^{10}BO. All values in cm^{-1}.

	H – ^{11}BO		H – ^{10}BO		D – ^{11}BO		D – ^{10}BO	
No.	exp.	cal.	exp.	cal.	exp.	cal.	exp.	cal.
1	(2849)[c]	3090.7 [2982][d]	(2874)[c]	3116.8	2259	2460.4	2303	2515.5
2	1817	1932.7 [1821][d]	1855	1974.5	1648	1752.5	1663	1767.0
3	754	861.8 [799][d]	764	872.6	606	694.4	617	707.7

Table 5. Calculated and experimental isotopic shifts[e]. All values in cm^{-1}.

	[ν(H – ^{10}BO) – ν(H – ^{11}BO)]		[ν(D – ^{10}BO) – ν(D – ^{11}BO)]	
No.	exp.	cal.	exp.	cal.
1	25	26.1	44	55.1
2	38	41.8	15	14.5
3	10	10.8	11	13.3
	[ν(H – ^{11}BO) – ν(D – ^{11}BO)]		[ν(H – ^{10}BO) – ν(D – ^{10}BO)]	
No.	exp.	cal.	exp.	cal.
1	590	630.3	571	601.3
2	169	180.2	192	207.5
3	148	167.4	147	164.9

The calculated isotopic shifts, together with the experimental values, are listed in Table 5. Although the calculated isotopic shifts are on the average 10% too high, the correlation between calculated and experimental values is excellent[e].

For H_3C – BO (C_{3v}) one expects twelve genuine vibrations, four of which being of A_1 and four (twofold degenerate) of E symmetry. The vibrational frequencies for the ^{11}B and ^{10}B isotopomers are listed in Table 6. The line spectra are plotted in Figure 4 and the cartesian displacement vectors belonging to A_1 are shown in Figure 5.

The strongest isotopic shift was calculated for the vibration 3 (cf. Figure 5) at 2112.5 cm^{-1} (H_3C – ^{11}BO) which is mainly due to a stretching of the BO bond. Under exchange of ^{11}B by ^{10}B this absorption is displaced to 2183.2 cm^{-1}, corresponding to an isotopic shift of 70.7 cm^{-1}.

The vibration predominantly due to stretching of the BO bond occurs at higher wavenumbers in H_3C – BO than in H – BO (e.g. 2112.5 cm^{-1} in H_3C – ^{11}BO and 1932.7 cm^{-1} in H-^{11}BO).

Table 6. 4-31G vibrational frequencies of H_3C-BO (all values in cm^{-1}).

$H_3C-{}^{11}BO$	$H_3C-{}^{10}BO$
A_1	
3173.1 (2)	3173.2 (2)
2112.5 (3)	2183.2 (3)
1541.2 (5)	1541.2 (5)
860.9 (7)	863.2 (7)
E	
3251.7 (1)	3251.7 (1)
1617.3 (4)	1617.6 (4)
1052.6 (6)	1061.2 (6)
384.0 (8)	394.6 (8)

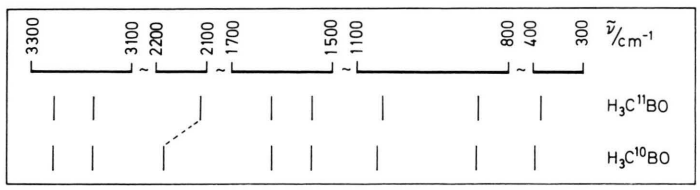

Fig. 4. Schematic representation of the calculated vibrational spectra of $H_3C-{}^{11}BO$ and $H_3C-{}^{10}BO$.

However, due to the different substituents at the boron atom these two vibrations are not directly comparable to each other and therefore do not allow any judgement regarding the BO bond strengths in these two molecules. Comparing the BO stretching force constants in both molecules a somewhat higher value is found for the BO bond in H – BO (H – BO: $k = 15.5$ mdyn/Å[f], H_3C-BO: $k = 14.9$ mdyn/Å; experimental values given for H – BO are 13.86, 13.83, and 14.32 mdyn/Å [1] and 14.29 mdyn/Å [12]). Accordingly, the curvature of the potential curve in its minimum is stronger for oxoborane than for methyloxoborane (cf. Figure 6). Similarily, at all levels of theory employed here, the BO bond distance is somewhat larger in H_3C-BO (4-31G: 120.4 pm) than in H – BO (4-31G: 119.9 pm). The weaker BO bond in methyloxoborane can be understood as follows: the orbitals of π symmetry of the methyl group mix with the π* MOs of the BO group and in this way introduce some antibonding character. At all levels of theory employed here, the methyl group is a π electron donor: according to all calculations the BO group of methyloxoborane carries a negative π charge (cf. Table 3).

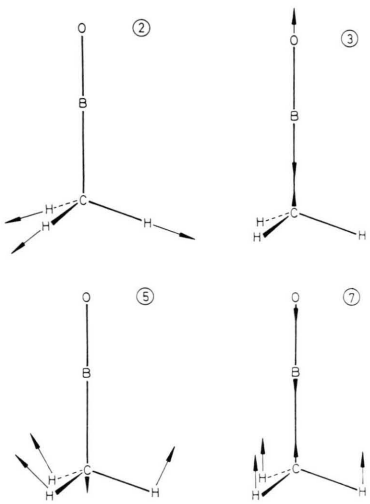

Fig. 5. A_1 normal modes of $H_3C-{}^{11}BO$.

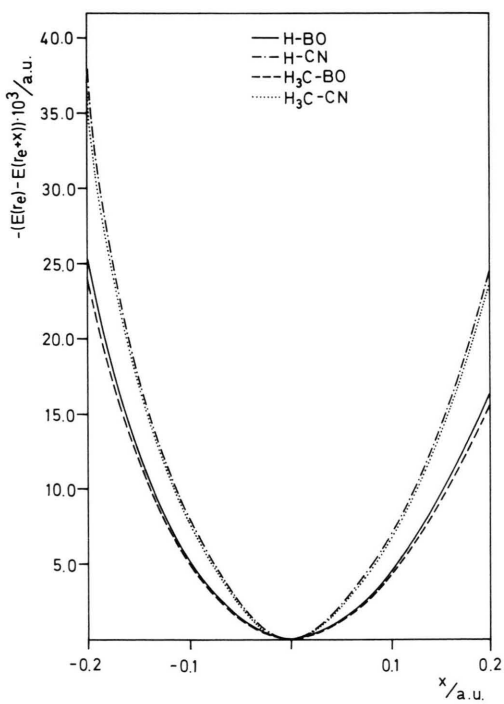

Fig. 6. Potential curves of the XY bonds in H – BO, H – CN, H_3C-BO, and H_3C-CN in the vicinity of the equilibrium bond distance (r_e). The energies are relative to the equilibrium value ($E(r_e)$).

The somewhat stronger BO bond in H – BO is also reflected by the change of energy associated with the isodesmic oxygen transfer reaction

$$H_3C\text{-}B + H\text{-}BO \longrightarrow H_3C\text{-}BO + H\text{-}B$$

which is 33.6 kJ/mol at the STO-3G and 14.4 kJ/mol at the 4-31G level. Total energies and geometries (closed shell singlets) of H – B and H_3C – B are listed in Table 12 of the appendix.

A similar situation is found for the pair H – CN/H_3C – CN[g]: according to 4-31G calculations the vibration which contains the strongest CN stretching contribution occurs at 2378.4 cm^{-1} in the case of H – CN and at 2577.4 cm^{-1} for H_3C – CN. The corresponding experimental values are 2096 cm^{-1} for H – CN [37] and 2266.7 cm^{-1} for H_3C – CN [38].

Regarding the force constants, stretching of the CN bond demands a higher amount of energy in the case of H – CN (k = 24.0 mdyn/Å[h]; experimental values are: k = 18.1 mdyn/Å [40], 18.707 mdyn/Å [41], 18.776 mdyn/Å [42], and 18.703 mdyn/Å [43]) than for H_3C – CN (k = 23.6 mdyn/Å; experimental value: k = 17.5 mdyn/Å [40]) (cf. Figure 6). Again, not only the CN bond length is larger in methylcyanide than in hydrocyanic acid but also the CN group in acetonitrile carries a negative π charge at all levels of theory, employed here (Table 3).

Whereas MNDO and an *ab initio* calculation at the STO-3G level led to small positive π charges for the NC group of H_3C – NC[g], a slightly negative value is obtained with the 4-31G basis set. At the same level the vibration with the strongest NC stretching contribution was calculated at 2412.0 cm^{-1} for H_3C – NC (experimental value: 2166 cm^{-1} [44]) whereas a value of 2248.9 cm^{-1} was obtained for H – NC (experimental value: 2029.2 cm^{-1} [45]).

Corresponding to the small π charge of the NC group in H_3C – NC, the NC stretching force constants are about the same for both molecules. The value for the methyl derivative is still a little bit smaller (calculated force constant: k = 20.6 mdyn/Å for H – NC, experimental value: k = 16.4 mdyn/Å [45] and calculated force constant k = 20.5 mdyn/Å for H_3C – NC; experimental value: k = 16.3 mdyn/Å [40]). However, neither the small π charge, nor the small difference between the two force constants should be overemphasized and the NC bond in H – NC and its methyl derivative should be considered as being of equal strength. It should be pointed out, however, that according to the 4-31G result, the NC bond length is somewhat shortened upon methyl substitution.

Softening[i] of the X – Y bond upon methyl substitution decreases in the order H_3C – BO > H_3C – CN > H_3C – NC. This order might be understood if one compares the 4-31G energies of the π* orbitals for the H – YX species in Table 7. The energy of these orbitals increase in the order H – BO < H – CN < H – NC. Consequently, the interaction between these molecular orbitals and the corresponding π orbitals of the methyl group should be the strongest in the case of H_3C – BO, whereas it should be of minor importance for H_3C – NC, which means that mixing of the π* into the π MOs is stronger in the former than in the latter case.

Comparing the σ charges ($q_\sigma(XY) = q(XY) - q_\pi(XY)$) of the XY groups in H – XY and H_3C – XY in Table 3 it is found that for XY = BO and CN these become positiver upon methyl sub-

Table 7. Orbital energies for molecules H – BO, H – CN, and H – NC obtained with STO-3G and 4-31G basis sets (all values in a.u.).

	STO-3G		
H – BO	H – CN	H – NC	
0.368449 (π*)	0.349514 (π*)	0.364957 (π*)	
0.368449 (π*)	0.349514 (π*)	0.364957 (π*)	LUMO
– 0.437777 (π)	– 0.441859 (π)	– 0.398355	HOMO
– 0.437777 (π)	– 0.441859 (π)	– 0.447722 (π)	
– 0.512397	– 0.493061	– 0.447722 (π)	
– 0.604067	– 0.748970	– 0.792055	
– 1.277968	– 1.181997	– 1.183159	
– 7.412248	– 11.079903	– 11.023288	
– 20.298797	– 15.384748	– 15.374849	
	4-31G		
H – BO	H – CN	H – NC	
0.170363 (π*)	0.199240 (π*)	0.204593 (π*)	
0.170363 (π*)	0.199240 (π*)	0.204593 (π*)	LUMO
– 0.517128 (π)	– 0.500894 (π)	– 0.477643	HOMO
– 0.517128 (π)	– 0.500894 (π)	– 0.517279 (π)	
– 0.609245	– 0.572226	– 0.517279 (π)	
– 0.672275	– 0.807178	– 0.878486	
– 1.345373	– 1.269832	– 1.277835	
– 7.648965	– 11.276461	– 11.284632	
– 20.535545	– 15.587176	– 15.574439	

stitution. This is also in accordance with a weaker XY bond in the methyl derivatives. Again, the pair $H-NC/H_3C-NC$ is the limiting case (Table 3): whereas, according to a calculation with a STO-3G basis set, the σ charge of the NC group in H_3C-NC is more positive than in $H-NC$, just the opposite emerges from our 4-31G and MNDO results. Calculation of the total XY Mulliken overlap populations for H_3C-XY and $H-XY$ demonstrates the strong basis set dependence of these numbers. So, for example, the total XY overlap populations obtained with the 4-31G basis set are higher in the case of the methyl derivatives (cf. Table 8). Contrarily, in accordance with our other results, employing the STO-3G basis set for the hydrogen compounds higher XY overlap populations are obtained than for the methyl derivatives.

Table 8. Mulliken total XY overlap populations in $H-XY$ and H_3C-XY.

Molecule	4-31G	STO-3G
H – BO	1.3239	1.1676
H_3C – BO	1.3542	1.1609
H – CN	1.6431	1.4751
H_3C – CN	1.7532	1.4628
H – NC	0.9159	1.3133
H_3C – NC	1.0281	1.3018

The *ab initio* orbital energies of the methyl derivatives considered are given in Table 9. For the pairs $H-BO/H_3C-BO$ and $H-CN/H_3C-CN$ the frontier orbitals are of π symmetry. The situation is different in the case of $H-NC$ and H_3C-NC. Whereas the LUMO is a degenerate π^* orbital for both molecules, too, the HOMO however, is of σ symmetry with its largest coefficient at the terminal carbon atom. A corresponding result for $H-NC$ was obtained employing a basis set of double zeta quality [14]. In both cases this orbital might be considered as a carbon lone pair. The exceptional character of $H-NC$ and H_3C-NC among the molecules considered here is also reflected by the response of the first vertical ionization potential upon methylation, which is different

Table 9. Orbital energies for molecules H_3C-BO, H_3C-CN, and H_3C-NC obtained with STO-3G and 4-31G basis sets (all values in a. u.).

H_3C-BO		STO-3G H_3C-CN		H_3C-NC		
0.382473 }	3e (π^*)	0.361459 }	3e (π^*)	0.370009 }	3e (π^*)	LUMO
0.382473 }	(π^*)	0.361459 }	(π^*)	0.370009 }	(π^*)	
−0.412643 }	2e (π)	−0.407264 }	2e (π)	−0.381561	$7a_1$	HOMO
−0.412643 }	(π)	−0.407264 }	(π)	−0.407977 }	2e (π)	
−0.481088	$7a_1$	−0.466954	$7a_1$	−0.407977 }	(π)	
−0.540425	$6a_1$	−0.591383 }	1e (π)	−0.603838 }	1e (π)	
−0.551944 }	1e (π)	−0.591383 }	(π)	−0.603838 }	(π)	
−0.551944 }	(π)	−0.639806	$6a_1$	−0.675409	$6a_1$	
−0.933297	$5a_1$	−0.983744	$5a_1$	−0.969170	$5a_1$	
−1.259095	$4a_1$	−1.166826	$4a_1$	−1.192038	$4a_1$	
−7.396929	$3a_1$	−11.064320	$3a_1$	−10.999156	$3a_1$	
−11.045527	$2a_1$	−11.112854	$2a_1$	−11.142278	$2a_1$	
−20.269675	$1a_1$	−15.350234	$1a_1$	−15.368641	$1a_1$	

H_3C-BO		4-31G H_3C-CN		H_3C-NC		
0.196101 }	3e (π^*)	0.208098 }	3e (π^*)	0.209896 }	3e (π^*)	LUMO
0.196101 }	(π^*)	0.208098 }	(π^*)	0.209896 }	(π^*)	
−0.492074 }	2e (π)	−0.465247 }	2e (π)	−0.458060	$7a_1$	HOMO
−0.492074 }	(π)	−0.465247 }	(π)	−0.468773 }	2e (π)	
−0.573995	$7a_1$	−0.548013	$7a_1$	−0.468773 }	(π)	
−0.604699 }	1e (π)	−0.630141 }	1e (π)	−0.641917 }	1e (π)	
−0.604699 }	(π)	−0.630141 }	(π)	−0.641917 }	(π)	
−0.616345	$6a_1$	−0.696065	$6a_1$	−0.738435	$6a_1$	
−1.002941	$5a_1$	−1.043953	$5a_1$	−1.034447	$5a_1$	
−1.324123	$4a_1$	−1.252605	$4a_1$	−1.279295	$4a_1$	
−7.632295	$3a_1$	−11.260724	$3a_1$	−11.258507	$3a_1$	
−11.228784	$2a_1$	−11.266165	$2a_1$	−11.278403	$2a_1$	
−20.513217	$1a_1$	−15.559519	$1a_1$	−15.567864	$1a_1$	

Table 10. Influence of methyl substitution on the first vertical ionization potential. The values listed are $E_{HOMO}(H_3C-XY) - E_{HOMO}(H-XY)$. All values in eV.

Pair	4-31G	STO-3G
$H-BO/H_3C-BO$	0.68	0.68
$H-CN/H_3C-CN$	0.97	0.94
$H-NC/H_3C-NC$	0.53	0.46

from those found for the pairs $H-BO/H_3C-BO$ and $H-CN/H_3C-CN$ (see below). According to the MNDO method, and different from the *ab initio* results, the HOMO of H_3C-NC is of π symmetry, too.

Following Koopmans' theorem [46], the ionization potentials are the negative orbital energies. The effect of methyl substitution on the first vertical ionization potential can be seen from the numbers in Table 10, where the differences between the energies of the frontier orbitals for each pair $H-XY/H_3C-XY$ are listed.

Knowledge of the approximate values of the vertical ionization potentials is of great importance for the identification of highly reactive intermediates by means of their photoelectron spectra. Ionization potentials of $H-BO$ have therefore been calculated by several authors employing various methods [11, 12, 18]. The highest value for $H-BO$ (14.66 eV) in this work was obtained with the semiempirical MNDO method and the lowest (11.91 eV) with the STO-3G basis set. The 4-31G value (14.07 eV) is closer to the MNDO than to the STO-3G result. The STO-3G and the 4-31G values bracket CEPA (13.1 eV) and PNO-CI (12.8 eV) results [12]. Other values reported are 14.06 eV, 14.25 eV, 13.61 eV, 13.11 eV, 13.76 eV, 13.36 eV [18], and 14.29 eV [11].

According to the *ab initio* calculations with both basis sets used here, the decrease of the first vertical ionization potential upon methylation increases from $H-BO/H_3C-BO$ to $H-CN/H_3C-CN$ by about 0.3 eV (cf. Table 10). The energies of the highest occupied molecular orbitals of $H-BO$ and $H-CN$ are very similar and differ by 0.44 eV (4-31G) and 0.11 eV (STO-3G) only. However, the energetical order obtained with the 4-31G basis set is different from the STO-3G result: employing the larger basis set the HOMO energy of $H-BO$ is lower than that of $H-CN$ whereas just the opposite order emerges from an STO-3G calculation (cf. Table 7). This clearly shows that it is not predominantly the energetical difference between the highest occupied molecular orbitals which causes the differences in the response to methyl substitution. Checking the CX bond lengths in H_3C-XY reveals a larger value for H_3C-BO (4-31G: 145.5 pm in H_3C-CN and 152.8 pm in H_3C-BO) (cf. Table 2). The difference between the CX bond lengths in H_3C-BO and H_3C-CN obtained with the 4-31G (STO-3G) basis set is 7.3 pm (5.9 pm). Therefore, due to a higher absolute value of the following element of the Fock matrix (see formula in [47])

$$\langle \pi(CH_3) | F(H_3C-XY) | \pi(H-XY) \rangle$$

the perturbation of the π orbitals by the appropriate orbitals of the methyl group should be stronger for H_3C-CN than for H_3C-BO ($\pi(CH_3)$ and $\pi(H-XY)$ are the MOs of π symmetry in methane and $H-XY$, respectively, whereas $F(H_3C-XY)$ is the Hartree-Fock operator of H_3C-XY). For the energy of the methyl group π orbital Houk et al. [47] suggest a value of approximately -14.2 eV. This value is essentially identical with the energy of the orbitals of π symmetry in methane, obtained with the STO-3G basis set ($E_{tot} = -39.726864$ a.u., $r(C-H) = 108.3$ pm). The corresponding 4-31G eigenvalue is -14.8218 eV ($E_{tot} = -40.139756$ a.u., $r(C-H) = 108.3$ pm).

Due to the σ lone pair character of the HOMO the decrease of the first vertical ionization potential upon methylation is the smallest for H_3C-NC. This is in accordance with experimental data for ionization from σ lonepairs in other compounds and might easily be understood by simple perturbational arguments [47].

Appendix

Table 11. 4-31G vibrational frequencies for H_3C-CN and H_3C-NC (all values in cm^{-1}).

H_3C-CN		H_3C-NC
	A_1	
3199.3 (2)		3199.0 (2)
2577.4 (3)		2412.0 (3)
1600.8 (5)		1629.1 (5)
982.6 (7)		1008.9 (7)
	E	
3278.0 (1)		3278.3 (1)
1638.3 (4)		1660.6 (4)
1211.8 (6)		1287.8 (6)
433.5 (8)		343.2 (8)

Table 12. Total energies and geometries of H – B and H_3C – B. Energies in a.u., bond lengths in pm, and bond angles in degrees.

Molecule		Total energy	Geometry
H – B	STO-3G	– 24.752986	r(B – H) = 121.2
	4-31G	– 25.076901	r(B – H) = 123.4
H_3C – B	STO-3G	– 63.364677	r(C – H) = 108.6 r(B – C) = 159.0 <HCH = 108.1 <HCB = 110.8
	4-31G	– 64.090283	r(C – H) = 108.8 r(B – C) = 156.8 <HCH = 107.9 <HCB = 111.0

Acknowledgement

We are thankful to Prof. Dr. P. Paetzold for stimulating this investigation. The authors greatfully acknowledge financial support by the Fonds der Chemischen Industrie and the computing time provided by the Rechenzentrum der Rheinisch-Westfälischen Technischen Hochschule Aachen.

[a] A microwave study [6] revealed that this molecule is a five-membered ring of C_{2v} symmetry. For the controversy about the structure of this compound and possible isomers see [2 – 8].

[b] *Ab initio* calculations for H – BO using the 4-31G basis set have also been performed by Summers and Tyrell [19].

[c] The H – B stretching frequency in H – BO was too weak for detection. The values given in parenthesis have been calculated from the experimental DBO force constant [1].

[d] These values have been calculated with a 6-31G* basis set [17]. Correlation effects have been included via second order Møller Plesset perturbation theory.

[e] The correlation between experimental and calculated isotopic shifts is: $\Delta\nu_{exp.} = 0.945\ \Delta\nu_{cal.} - 3.041$; $|r| = 0.9998$.

[f] This result might be compared with a CEPA-2 value of 15.29 mdyn/Å [12]. Another calculated value for the BO stretching force constant in H – BO is k = 15.538 mdyn/Å [11].

[g] We are not aware of published vibrational frequencies of H_3C – CN and H_3C – NC [34], obtained with the 4-31G basis set. The corresponding values are therefore given in Table 11 of the appendix.

[h] Working with the same basis set, Curtiss and Pople [39] obtained a CN stretching force constant and vibrational frequencies (k = 23.6 mdyn/Å; 3695 cm^{-1}, 2384 cm^{-1}, 911 cm^{-1}) which slightly differ from our results (k = 24 mdyn/Å; 3662 cm^{-1}, 2378 cm^{-1}, 911 cm^{-1}). This is most likely due to the fact that the force constant matrix in [39] had been calculated completely numerically.

[i] "Softening" means that the difference between the XY stretching force constants k(H – XY)-k(H_3C – XY) is positive.

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