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Charge Distribution in Alkylboranes and Alkylamines and their Adducts with NH_3 and BH_3 respectively, as Calculated by Different Methods

WOLFGANG LINERT, VIKTOR GUTMANN

Institute of Inorganic Chemistry, The Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria

and PETER G. PERKINS

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U. K.

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The charge distribution in alkylboranes and alkylamines and in their adducts with NH_3 and BH_3, respectively, has been calculated by four different methods, namely, the CNDO–MO–SCF method, the Jolly and Perry procedure, the MNDO method and the modified Sanderson method. All of them gave reasonable results for the isolated alkyl compounds. For the adducts, fair agreement between calculated results and experience was obtained only by the modified Sanderson method. Neither the CNDO–MO–SCF nor the MNDO method leads to spillover and pile-up effects at the acceptor atom and at the donor atom, respectively, or to the chain-terminating effect. For the CNDO–MO–SCF method, this may be due to the changes in internuclear positions produced by the strong donor–acceptor interactions being neglected. For the MNDO method, however, this reason is not valid. The failure of the Jolly and Perry method may be due to its assumption of formal charge: this involves differentiating between a covalent and a coordinate bond.

Introduction

As an interaction between two molecules generally involves charge transfer, it may be considered as a donor–acceptor interaction in the widest sense of the word [1]. Two different contributions which are considered in quantum chemical calculations are the effects of charge transfer and polarisation, which cannot be unambiguously separated. In the course of the formation of an adduct, the charge density patterns of the reacting molecules mutually interpenetrate and reorganise to a new overall pattern for the new molecule. Although the so-called partial charge of an atom in a molecule cannot be defined unambiguously, comparisons of the results of quantum chemical calculations for reactants and reaction products have proved to be of great qualitative value to chemists, since trends in the changes of the charge-density pattern are produced.

An entirely different approach to the problem has been provided by the consideration of the bond-length-variation rules and the empirical parameters of the extended donor–acceptor approach [1]. A donor–acceptor interaction is found to lead to lengthening of the bonds adjacent to the site of the interaction, *i.e.*, of the bonds adjacent to the donor- and acceptor-atom, respectively. Thus, the so-called Goldschmidt rule according to which the bonds in crystals become longer the greater the coordination number, is generally valid.

Increase in bond length may be associated with increase in bond polarity [2] and, hence, the negative charge at the donor atom and the positive charge at the acceptor atom should be increased. The conventional view is that the polarity of a D–A bond is in the sense $\overset{+}{D}-\overset{-}{A}$, but there is now sufficient evidence available, from the results of measurements [1, 3–9] as well as those of various quantum chemical calculations [10–15], that the 'initial' loss of negative charge at the donor-atom (D) is over-compensated by intramolecular charge transfer within the donor-unit towards the donor-atom. Concomitantly, the gain in negative charge at the acceptor atom (A) is passed on to other parts in the acceptor unit, including possibly a portion of the negative charge that resided originally at the acceptor atom in the free acceptor unit. These facts have been called the *pile-up effect* of negative charge at the donor-atom and the *spillover effect* of negative charge at the acceptor-atom [1, 16].

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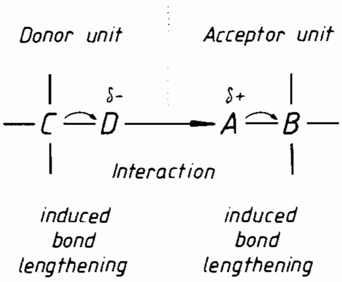
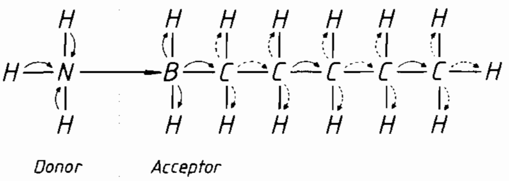
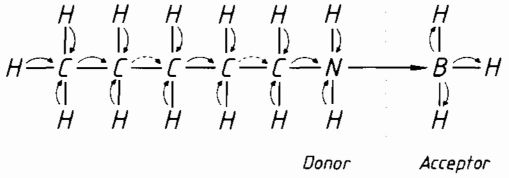


The redistribution of the charges within the new molecule leads, in most cases, to alternating changes in the partial changes of the subsequent atoms [1, 17]. Such changes are less pronounced the greater the distance from the site of the donor–acceptor interaction, and they may be unmeasurably small in the regions which are remote from the former. It appears, however, that the effects are more pronounced at the positions by which the new system is terminated [18, 19]. It has also been said [1] that the donor properties originally exhibited at the donor atom of the donor component have been partly distributed over those atoms which are in the positions by which the acceptor unit is terminated; the acceptor properties originally exhibited at the acceptor atom of the acceptor unit have been partly distributed over the atoms terminating the donor unit in the adduct.





It was, therefore, of interest to learn in what ways these results could be underpinned by various theoretical approaches. As model compounds, alkylboranes and alkylamines with linear arrangements of up to 10 carbon atoms were chosen. The charge distribution was calculated by the following methods: the CNDO–MO–SCF method [20], the MNDO method [21], the method according to Jolly and Perry [22, 23], and the Sanderson method modified by Craver *et al.* [24]. These methods were also applied to the calculations for the NH_3- and BH_3-adducts of the said compounds.

Methods of Calculation

For the quantum chemical calculations within the usual CNDO–MO–SCF framework [20] the input parameters used have been described in the literature [25]. The geometries around the boron atom in BH_3 and BH_2R are changed by adduct formation from a planar to a distorted tetrahedral environment. For the free alkylboranes, calculations were performed for the planar as well as for the idealised tetrahedral arrangements The molecular geometrical data (which are not varied in this method) were abstracted from standard compilations [26]. The element $P_{\lambda\sigma}$ of the density matrix P was obtained according to the relation,

$$P_{\lambda\sigma} = \sum_i 2C_{i\lambda}C_{i\sigma} \tag{1}$$

where $C_{i\lambda}$ and $C_{i\sigma}$ are the coefficients of the atomic orbitals λ and σ in the occupied molecular orbital *i*. The charge Q on an atom in the molecule is defined by,

$$Q = n - \Sigma P_{\lambda\lambda} \tag{2}$$

where the summation runs over all occupied atomic orbitals of the atom and *n* is the number of valence electrons in the atom.

The MNDO results were derived from single-determinant MNDO [21, 27] calculations, without inclusion of configuration interactions. The geometrical structures were optimised by the Davidson–Fletcher–Powell method [28, 29].

According to the so-called Jolly and Perry method [22, 23], the charge-dependent orbital electronegativities are defined for each of the hybrid bonding orbitals represented in the valence bond structure. From the condition of electronegativity equalisation, one obtains:

$$\frac{b(h_m + h_n)}{(N_{nm})^a} q_{mn} + h_m \sum_{i \neq n} q_{mi} - h_n \sum_{i \neq m} q_{ni} =$$

$$= \chi(p)_n - \chi(p)_m + \frac{S_{nm}}{(N_{nm})^a} [\chi(s)_n - \chi(p)_n] -$$

$$- \frac{S_{mn}}{(N_{nm})^a} [\chi(s)_m - \chi(p)_m] + c(h_n F_n - h_m F_m) \tag{3}$$

Here, $\chi(s)$, $\chi(p)$ are orbital electronegativities from Hinze and Jaffe [30, 31], h_m and h_n are proportional to the orbital-ionization potentials and orbital electron-affinities [30, 31]. S_{nm} is the s-character of σ-orbitals given as the reciprocal value of the sum of the σ-bond orbitals and the non-bonding orbitals, q_{nm} is the charge transferred from atom *n* to atom *m*,

TABLE I. Results of Charge Calculations for BH_3, NH_3, H_3NBH_3, and their CH_3- and C_2H_5-Derivates.

Atom	CNDO-Method	MNDO-Method	Jolly and Perry Method	Modified Sanderson Method
		BH_3		
B	0.025	0.228	0.079	0.127
H	–0.008	–0.076	–0.026	–0.042
		NH_3		
N	–0.254	–0.503	–0.211	–0.165
H	0.085	0.168	0.070	0.055
		$H_3N–BH_3$		
N	–0.133	–0.067	–0.036	–0.183
H	0.158	0.151	0.204	0.015
B	–0.153	–0.247	0.173	0.148
H	–0.062	0.090	–0.137	0.024
		$BH_3–CH_3$		
B	0.05	0.143	0.098	0.13
H_B	–0.04	–0.072	–0.025	–0.039
C	–0.20	–0.043	–0.059	–0.06
H_C	0.09	+0.021	0.013	0.00
		$BH_3–CH_2–CH_3$		
B	0.054	0.153	0.10	0.13
H_B	–0.033	–0.070	–0.03	–0.038
C_1	–0.127	–0.091	–0.074	–0.056
H_{C_1}	0.08	0.028	0.01	0.00
C_2	–0.095	0.042	–0.049	–0.048
H_{C_2}	0.034	0.008	0.015	0.012
		$BH_3–NH_2–CH_3$		
B	–0.220	–0.230	–0.163	0.149
H_B	–0.050	–0.092	–0.138	–0.023
N	–0.045	0.011	–0.037	–0.180
H_N	0.111	0.151	0.804	0.038
C	–0.031	0.109	0.123	–0.039
H_C	0.073	0.033	0.027	0.021
		$BH_3–NH_2–CH_2–CH_3$		
B	–0.222	–0.230	–0.163	0.149
H_B	–0.052	–0.094	–0.138	–0.023
N	–0.056	0.018	0.036	–0.179
H_N	0.104	0.150	0.024	0.038
C_1	0.035	0.056	0.135	0.036
H_{C_1}	0.062	0.054	0.028	0.024
C_2	–0.101	0.011	–0.036	–0.043
H_{C_2}	0.048	0.008	0.016	0.017
		$NH_2–CH_3$		
N	–0.153	–0.501	0.203	–0.161

(continued overleaf)

TABLE I. *(continued)*

Atom	CNDO-Method	MNDO-Method	Jolly and Perry Method	Modified Sanderson Method
H_N	0.041	0.172	0.071	−0.059
C	−0.055	0.242	0.003	−0.034
H_C	0.042	−0.037	0.002	0.264
		$NH_2-CH_2-CH_3$		
N	−0.164	−0.274	−0.202	−0.160
H_N	0.037	0.094	0.071	0.060
C_1	0.016	0.072	0.015	−0.031
H_{C_1}	0.374	−0.025	0.020	0.029
C_2	−0.100	0.031	−0.043	−0.431
H_{C_2}	0.042	−0.005	0.016	0.018
		$H_3N-BH_2-CH_3$		
N	−0.111	0.065	−0.035	−0.182
H_N	0.136	0.150	0.020	0.035
B	−0.028	−0.278	−0.136	0.146
H_B	−0.075	−0.019	−0.136	−0.026
C	−0.203	0.480	−0.188	−0.055
H_C	0.012	−0.049	0.006	0.005

F_n is the formal charge of the atom, N_{nm} is the bond order.

By solving the *n*-equations the *n* unknown q_{ij}-values were obtained. The charge on atom *i* is then given by

$$Q_i = F_i + \sum_i q_{ij} \qquad (4)$$

In the original Sanderson method [32] and its modifications [24], the equalised electronegativity is approximated by

$$\bar{\chi} = \sqrt[n]{\prod_i^n \chi_i} \qquad (5)$$

where the χ_i are the electronegativities or stability ratios of the atoms or of atomic groups [32]. The partial charges Q_i are given in both the original and the modified method by

$$Q_i = (\bar{\chi} - \chi_i)/\Delta\chi_i \qquad (6)$$

where $\Delta\chi_i$ is a normalising factor usually taken as $2.08\sqrt{\chi_i}$. In order to adapt this model to the structure of the molecules investigated, Craver *et al.* [24] modified the method of Sanderson. According to this method, the partial charge on an atom in a molecule is obtained from a group stability ratio (or group electronegativity)$\bar{\chi}_g$ as calculated for the atom and for the groups surrounding it. $\bar{\chi}_g$ is used instead of χ_i in eqn. (5). The group for which $\bar{\chi}_g$ is defined is the atom of interest (central atom) and all sub-groups directly bound to it. These sub-groups can be terminal atoms (bonded only to the central atom) or other groups of atoms.

For the calculations by the CNDO–MO–SCF and the Jolly–Perry method, computer programs for the Cyber 74 computer of the Technical University of Vienna were available. The MNDO calculations were carried out at the Institute for Theoretical and Radiation Chemistry of the University of Vienna.

Results and Discussion

The results of the charge calculation for BH_3, NH_3 and the adduct H_3NBH_3 and of their CH_3- and C_2H_5-derivatives are given in Table I and the eigenvalues as obtained by the CNDO–MO–SCF method for BH_3, NH_3, and NH_3BH_3 in Table II. For longer alkylboranes, alkylamines and their adducts with NH_3 and BH_3, the most characteristic results are summarised in simplified graphical form (Figs. 1–6) in which the results for the hydrogen atoms are not included. The lines between the points have been drawn in order to pick out the general pattern along the chains as obtained for molecules containing between 6 and 10 carbon atoms.

TABLE II. Molecular Orbital Energies of BH_3, NH_3, NH_3-BH_3 Eclipsed and NH_3-BH_3 Staggered, Calculated by Means of the CNDO/2 Method (*signifies that the orbital is occupied with 2 electrons).

BH_3		NH_3	
MO-energy [eV]	Degree of degeneration	MO-energy [eV]	Degree of degeneration
−27.23	1*	−37.70	1*
−13.89	2*	−14.14	1*
3.94	1	−13.54	1*
9.57	1	−11.65	1*
9.69	2	11.34	
		11.43	
		11.86	

H_3N-BH_3 eclipsed		H_3N-BH_3 staggered	
MO-energy [eV]	Degree of degeneration	MO-energy [eV]	Degree of degeneration
−44.06	1*	−44.07	1*
−25.05	1*	−25.08	1*
−17.99	2*	−17.94	2*
−13.06	1*	−13.09	1*
−9.96	2*	−10.04	2*
8.20	1	8.19	1
9.37	2	9.37	2
9.48	1	9.46	1
11.19	2	11.18	2
		11.70	1

Using the four methods, essentially the same charge distributions were obtained only for the free BH_3, the alkylboranes, NH_3, and the free alkylamines. The inductive effects in alkylboranes due to the positive charge of the boron atom, and those in alkylamines due to the negative charge of the nitrogen atom, respectively, are reflected in the differences in charges of the C_1-atoms. The latter are negative in the alkylboranes (Figs. 1, 2, 3) and positive in the alkylamines (Figs. 4, 5, 6). As expected, the alternating differences in charges at the subsequent carbon atoms are found to be smaller the further the carbon atoms lie from the B- and N-atoms, respectively. These differences are in agreement with the experimental findings of the alternating differences in nucleophilic and electrophilic properties for the chain carbon atoms [1, 17, 18]: in alkylboranes the even-numbered carbon atoms have a larger positive charge (enhanced acceptor-properties) than the odd-numbered carbon atoms. In alkylamines the even-numbered carbon atoms are more negatively charged (enhanced donor-properties) than the odd-numbered carbon atoms. In agreement with the bond-length-

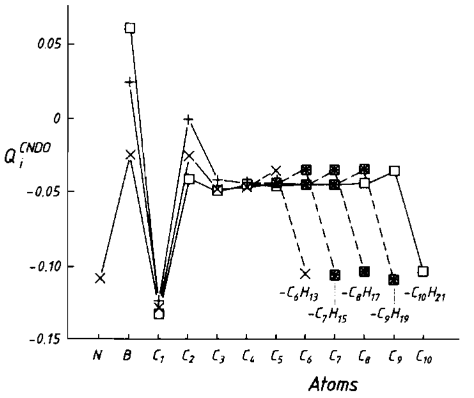


Fig. 1. Charge distribution in alkylboranes and their NH_3 adducts, calculated by the CNDO method; □, free alkylboranes, calculated for planar coordination around the β-atom; +, free alkylboranes, calculated for tetrahedral coordination around the β-atom; ×, NH_3-adduct.

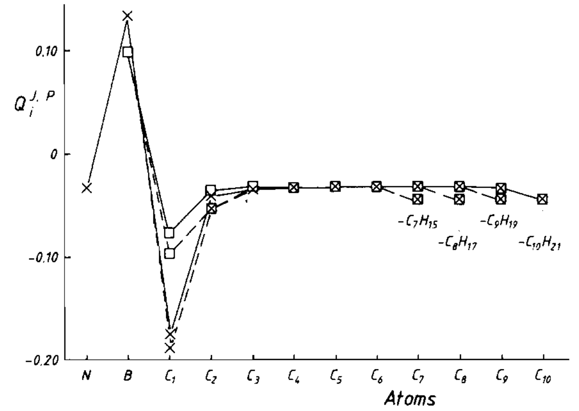


Fig. 2. Charge distribution in alkylboranes and their NH_3 adducts, calculated by the Jolly and Perry method; □, free alkylborane; ×, NH_3-adduct.

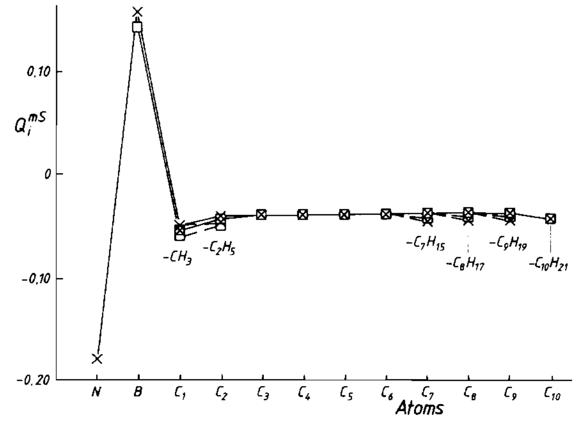


Fig. 3. Charge distribution in alkylboranes and their NH_3 adducts, calculated by the modified Sanderson method; □, free alkylborane; ×, NH_3-adduct.

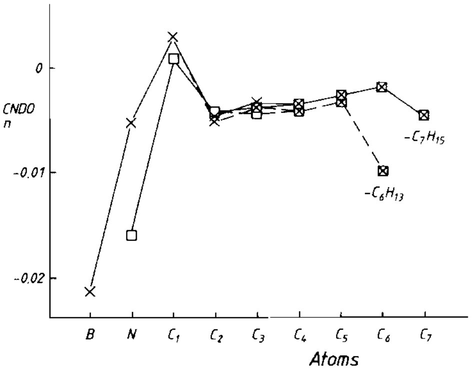


Fig. 4. Charge distribution in alkylamines and their BH_3 adducts, calculated by the CNDO method; □, free alkylamine; ×, BH_3-adduct.

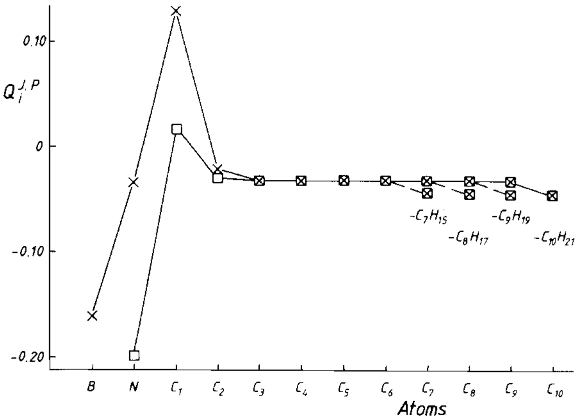


Fig. 5. Charge distribution in alkylamines and their BH_3 adducts, calculated by the Jolly and Perry method; □, free alkylamine; ×, BH_3-adduct.

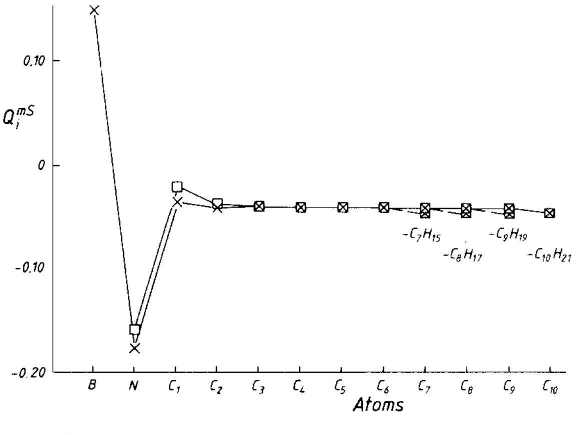


Fig. 6. Charge distribution in alkylamines and their BH_3 adducts calculated by the modified Sanderson method; □, free alkylamine; ×, BH_3-adduct.

variation rules [1], the effects noted are more strongly pronounced at the chain-terminating atoms but direct comparison is not justified, because of the different atomic environments. Consequently, the chain-terminating C-atoms in alkylboranes, which consist of an even number of carbon atoms, have higher positive charge than do those consisting of an odd number of carbon atoms. The charges at the terminating C-atoms are more negative in alkylboranes than in alkylamines.

The introduction of a BH_2-group (acceptor) at one end of a hydrocarbon leads to an increase in negative charge and, hence, in the donor-properties of the C-atom at the other end. On the other hand, the introduction of a NH_2-group (donor) leads to a decrease in negative charge at the other end of the chain and, hence, to acceptor-properties. These effects are most strongly pronounced in the results of the CNDO-method.

The changes which are expected to result from the donor-acceptor interactions are partly produced by the results of the modified Sanderson method. These show clearly an increase in the positive charge at the boron-atom in the NH_3-adducts (spillover effect) of the alkylboranes as well as an increase in negative charge at the nitrogen atom in alkylamines (pile-up effect) as compared with the free compounds (Table I, Figs. 3 and 6). These results are in qualitative agreement with results from *ab-initio* calculations of similar systems [33–35]. It has been shown that the Sanderson method, in many cases, agrees well with experimental data as obtained, for example, by ESCA- and Mössbauer measurements [24, 36].

Neither the spillover- nor the pile-up-effect was obtained by means of the CNDO- and the MNDO-method. Our calculations lead to B–N bond polarisation by assigning a negative charge to the B-atom and a positive charge to the N-atom. These results are in clear contradiction to those of the Sanderson method and the quoted *ab-initio* calculations. The CNDO-method used is not suitable for finding the correct internuclear distances in the adducts through an optimisation formalism. This means that the latter method is not flexible enough to account for changes induced within the molecules on adduct formation. However, neither were these effects found by the MNDO-method.

The semi-empirical calculations carried out according to Jolly and Perry also do not show the spillover and pile-up effects: this method involves explicitly a distinction between 'coordinate–covalent' bonds and 'normal' covalent bonds in referring to the use of formal charges. It is not clear whether such a distinction is physically meaningful.

Optimal internuclear distances resulting from the MNDO-method are given in Table III. In the adducts, the bonds adjacent to the sites of the donor–acceptor interaction appear to be lengthened. The C_1–H distances are shortened (according to the bond length variation rules [1]) but no significant changes are found for the C_2–H distances. In the alkylborane

TABLE III. Internuclear Distances, Calculated by Means of the MNDO-Method.

Compound	Internuclear Distance, Å							
	H–N	N–B	B–H	N–C_1	B–C_1	C_1–H	C_1–C_2	C_2–H
BH_3			1.155					
NH_3	1.007							
H_3B–NH_3	1.015	1.591	1.180					
BH_2CH_3			1.160		1.335	1.112		
H_3N–BH_2CH_3	1.015	1.600	1.186		1.582	1.112		
NH_2CH_3	1.008			1.460		1.118		
H_3B–NH_2CH_3	1.020	1.609	1.179	1.497		1.110		
$BH_2CH_2CH_3$			1.160		1.543	1.118	1.527	1.109
H_3N–$BH_2CH_2CH_3$	1.016	1.599	1.186		1.593	1.117	1.529	1.110
$NH_2CH_2CH_3$	1.009			1.467		1.120	1.534	1.109
H_3B–$NH_2CH_2CH_3$	1.020	1.609	1.179	1.503		1.117	1.536	1.109

TABLE IV. Free Enthalpies of Formation from the Atoms and Dipole Moments as Calculated by the MNDO-Method.

Molecule	ΔH [Kcal/Mol]	μ(calc.) [D]
BH_3	11.73	0.00586
NH_3	−6.30	1.70
H_3B–NH_3	−22.66	6.02
BH_2CH_3	−7.82	0.625
H_3N–BH_2CH_3	−35.64	5.8
NH_2CH_3	−7.5	1.48
H_3B–NH_2CH_3	−17.18	6.07
$BH_2CH_2CH_3$	−12.91	0.586
H_3N–$BH_2CH_2CH_3$	−39.64	5.74
$NH_2CH_2CH_3$	−13.50	1.43
H_3B–$NH_2CH_2CH_3$	−22.64	6.26

adducts the C_1–C_2 distances appear longer, but shorter in the alkylamine-adducts. Table IV gives further results of the MNDO-calculations, namely, for the enthalpies of formation from the atoms and the calculated dipole moments. The latter may be compared with the experimental dipole moments of NH_3, H_3N–BH_3, and NH_2CH_3; the values are 1.47, 4.92, and 1.31 D, respectively and, clearly, agreement with experiment is not particularly good.

We are forced to the conclusion that the MNDO method is, as yet, not sufficiently accurate to reproduce the subtle bond-shortening–lengthening phenomena associated with donor–acceptor bond formation.

Calculations were performed for these alkyl-compounds in order to study the influence of the C-chain length on the energies of the highest occupied molecular orbitals (HOMO) and the energies of the lowest unoccupied molecular orbital (LUMO). These are of interest, as relationships are known between HOMO-energies and donor numbers as well as LUMO-energies and acceptor numbers of solvents [37]. The results are presented in Table V.

The HOMO-energies and the LUMO-energies are lower the greater the chain length of the model compounds (with the exception of the free alkylboranes with the unrealistic assumption of tetrahedral coordination around the B-atom). A steady decrease in LUMO-energies is generally found with increase in chain length but, in the free alkylboranes, alternating differences in LUMO-energies are revealed in going from a molecule with N carbon atoms to a molecule with (N + 1) carbon atoms (Table V). This means that there is a stepwise enhancement of the acceptor-properties of the alkylboranes with an increase in chain length. Corresponding alternations were not found for HOMO-energies in the free alkylamines. HOMO- and LUMO-energies of the NH_3 adducts of the alkylboranes are higher than those in the free alkylboranes. The HOMO levels in the adduct of the alkylamines with BH_3 are not significantly changed, whereas their LUMO-energies are lowered.

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TABLE V.; Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) Energies [eV] of the Linear Alkylboranes with Planar (p) and Tetrahedral (t) Arrangements as well as of Alkylamines and Their NH_3 and BH_3 Adducts Calculated by the CNDO/2 Method.

Compound	HOMO	LUMO	Compound	HOMO	LUMO
$BH_2C_3H_7$ (p)	−7.692	4.707	$BH_2C_3H_7$ (t)	−7.467	3.989
$BH_2C_4H_9$ (p)	−7.280	4.689	$BH_2C_4H_9$ (t)	−7.269	3.996
$BH_2C_5H_{11}$(p)	−6.988	4.701	$BH_2C_5H_{11}$(t)	−7.105	4.027
$BH_2C_6H_{13}$(p)	−6.763	4.679	$BH_2C_6H_{13}$(t)	−6.973	4.015
$BH_2C_7H_{15}$(p)	−6.633	4.675	$BH_2C_7H_{15}$(t)	−6.765	4.020
$NH_3BH_2C_3H_7$	−6.349	7.075	$NH_2C_3H_7$	−8.395	8.224
$NH_3BH_2C_4H_9$	−6.217	7.036	$NH_2C_4H_9$	−7.989	7.972
$NH_3BH_2C_5H_{11}$	−6.101	6.998	$NH_2C_5H_{11}$	−7.603	7.882
$NH_3BH_2C_6H_{13}$	−6.002	6.960	$NH_2C_6H_{13}$	−7.152	7.812
$NH_3BH_2C_6H_{15}$	−5.901	6.928	$NH_2C_7H_{15}$	−6.690	7.756
$BH_3NH_2C_3H_7$	−8.184	6.962			
$BH_3NH_2C_4H_9$	−8.153	6.902			
$BH_3NH_2C_5H_{11}$	−8.129	6.902			
$BH_3NH_2C_6H_{13}$	−7.853	6.867			
$BH_3NH_2C_7H_{15}$	−6.989	6.829			

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References

1 V. Gutmann, 'The Donor–Acceptor Approach to Molecular Interactions', Plenum Press, New York (1978).
2 I. Lindqvist, 'Inorganic Adduct Molecules of Oxo-Compounds', Springer-Verlag, Berlin (1963).
3 W. S. Sensen, 'The Lewis Acid–Base Concepts, An Overview', Wiley, New York (1980) 135.
4 C. H. J. Wells, *Spectrochim. Acta, 22,* 2125 (1966).
5 J. Yarwood, *Spectrochim. Acta, 26A,* 2099 (1970).
6 E. T. Strom, W. L. Orr, B. Snowden and D. E. Woessner, *J. Phys. Chem., 71,* 4017 (1967).
7 G. A.Bowmaker and S. Hacobian, *J. Austral. Chem., 22,* 2047 (1969).
8 S. Ichiba, H. Sakai, H. Negita and Y. Maeda, *J. Chem. Phys., 54,* 1627 (1971).
9 K. Burger and E. Fuck, *Inorg. Nucl. Chem. Letters, 10,* 171 (1974).
10 E. Clementi, *J. Chem. Phys., 46,* 3851 (1967).
11 L. A. Carreira and W. B. Person, *J. Am. Chem. Soc., 94,* 1485 (1972).
12 M. I. Baraton, J. Gerbier and S. Besnaionou, *C.R. Acad. Sci. Paris, B276,* 797 (1973).
13 L. Leroy and G. Louterman-Leloup, *J. Mol. Structure, 28,* 33 (1975).
14 L. Leroy, G, Louterman-Leloup, J. Gaultier and M. Schroer, *J. Mol. Structure, 25,* 205 (1975).
15 B. M. Rode, *Chem. Phys. Lett., 32,* 38 (1975).
16 V. Gutmann, *Rev. Roum. Chim., 22,* 679 (1977).
17 D. Seebach, *Angew. Chem., 91,* 259 (1979).
18 H. Singh and J. M. Tedder, *J. Chem. Soc. London B,* 605 (1966).
19 V. Gutmann, G. Resch and W. Linert, *Coord. Chem. Revs.,* in the press.
20 D. R. Armstrong, P. G. Perkins and J. J. P. Stewart, *J. Chem. Soc. London, 23,* 3674 (1971).
21 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc., 99,* 4899 (1977).
22 W. L. Jolly and W. B. Perry, *J. Am. Chem. Soc., 95,* 5442 (1973).
23 W. L. Jolly and W. B. Perry, *Inorg. Chem., 13,* 2686 (1974).
24 J. C. Craver, R. C. Gray and D. M. Hercules, *J. Am. Chem. Soc., 96,* 6851 (1974).
25 K. A. Levison and P. G. Perkins, *Theor. Chim. Acta, 14,* 206 (1969).
26 'Tables of Interatomic Distances and Configurations in Molecules and Ions', Chem. Soc. Special Publication No. 11, London, 1958.
27 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc., 99,* 4907 (1979).
28 R. Fletcher and M. J. D. Powell, *Comput. J., 6,* 136 (1963).
29 W. C. Davison, *J. Am. Chem. Soc., 10,* 406 (1968).
30 J. Hinze and H. H. Jaffe, *J. Am. Chem. Soc., 84,* 540 (1962).
31 J. Hinze and H. H. Jaffe, *Can. J. Chem., 41,* 1315 (1963); *J. Phys. Chem., 67,* 1501 (1963).
32 R. T. Sanderson, 'Chemical Bond and Bond Energy',

2nd ed. Phys. chem. Series of Monographs, Acad. Press, New York, 1976.
33 D. R. Armstrong and P. G. Perkins, *J. Chem. Soc. (A), 2,* 1044 (1969).
34 D. R. Armstrong and P. G. Perkins, *J. Chem. Soc. (A), 2,* 2566 (1969).
35 A. Veillard et B. Levy, R. Deudol and F. Gelieis, *Theor. Chim. Acta, 8,* 312 (1967).
36 W. Linert, G. Wiesinger, O. Baumgartner and V. Gutman, to be published.
37 A. Sabatino, G. LeManne and L. Paoloni, *J. Phys. Chem., 84,* 2641 (1980).