The Use of Quantum-Chemical Semiempirical Methods to Calculate the Lattice Energies of Organic Molecular Crystals. Part III: The Lattice Energy of Borazine ($B_3N_3H_6$) and its Packing in the Solid State*

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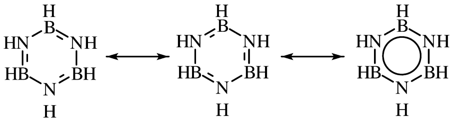
Dedicated to Professor Syd Hall, PhD, on the occasion of his 65th birthday

A previously presented quantum-chemical scheme has been used to calculate the lattice energies of borazine ($B_3N_3H_6$), the low pressure polymorph of benzene (C_6H_6), and of borazine in the low-pressure benzene lattice utilizing some frequently used semiempirical methods (CNDO/2, INDO, MINDO/3, MNDO, AM1, PM3, MSINDO). With all methods the lattice energy of the title compound was found to be less favourable than that of isoelectronic benzene, which offers an explanation of the significantly lower melting point of $B_3N_3H_6$. Calculation of the lattice energy of borazine in the crystal lattice of the low-pressure modification of benzene revealed that the interactions between the molecules in this environment are not so stabilizing as those in its own lattice. This is predominantly due to a less favourable contribution of the dispersion energy. The semiempirical results have qualitatively been confirmed by quantum-chemical calculations on small molecular clusters at the MP2/6-31+G*//HF/6-31+G* level of *ab initio* theory. In these calculations we assumed pairwise additivity of the intermolecular interactions and calculated the energy of interaction between a reference molecule and all those neighbours to which the shortest intermolecular distance does not exceed 3 Å.

Key words: Borazine; Lattice Energy; Calculations; Semiempirical Methods.

1. Introduction

Some physical properties of liquid borazine, such as the density, surface tension, and molecular weight, closely resemble those of the isoelectronic benzene. Moreover, like in the case of benzene, the first non-vanishing electric multipole is the quadrupole moment and, like in the case of benzene, it is possible to write canonical forms corresponding to a delocalized π system superimposed on the σ framework, so that, in spite of its completely different chemical properties, the title compound is often entitled "inorganic benzene" [1, 2].



Its remarkably lower index of refraction of $n_D{}^{20} = 1.3821$ [3, 4] (*vs.* $n_D{}^{20.2} = 1.5007$ of benzene [5]), however, reveals significantly different molecular features. "Experimental" molecular polarizabilities can approximately be calculated from the indices of refraction, densities, and molecular weights by means of the Lorenz-Lorentz equation. Assuming equal densities and molecular weights, the molecular polarizability decreases with decreasing index of refraction. Employing experimentally determined values for the densities of the liquids (d^{20}, borazine[a]: 0.8404 g·cm^{-3}, benzene: 0.8788 g·cm^{-3}), the indices of refraction mentioned above, and the molecular weights (borazine: 80.50, benzene: 78.11) one obtains "experimental" molecular polarizabilities of 8.84 Å^3 for borazine and 10.38 Å^3 for benzene. The vertical (Koopmans) ionization potentials calculated at the HF/6-31+G* level of *ab initio* theory are 11.128 eV for borazine and 9.173 eV for benzene, respectively[b]. Using the experimental values

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[a] The formula describing the temperature dependence of the density of borazine between 238.2 and 319.9 K given in [4] is at odds with the one published originally [8].

[b] E_{tot} (borazine) = −241.1612145 a. u., E_{tot} (benzene) = −230.7110925 a. u.

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of the molecular polarizabilities and the calculated ionization potentials together with the London formula for the dipole contribution to the dispersion energy, one obtaines dispersion coefficients[c] of $C_6 = 741.3$ eV·Å^6 for benzene and of 652.2 eV·Å^6 for borazine, which could explain the much lower boiling point of the latter compound (borazine: 55 °C, benzene: 80°C [1]).

These significantly different molecular features of benzene and borazine are not only reflected by differences between their physical and chemical properties but also by the crystal packing of borazin [2], that is different from those of the modifications of benzene studied so far experimentally [6, 7]. According to various quantum-chemical calculation methods the boron and the nitrogen atom of the ring carry high partial charges of opposite sign. Thus, *intuitively* one might expect that electrostatics play an important role and that the molecules are, for example, arranged coplanarly in stacks with nitrogen above boron, and *vice versa*. However, in the crystal lattice of borazine the rings are arranged in tilted stacks [2], and the shortest intermolecular distances involving only non-hydrogen atoms occur between atoms of the same kind (B···B; N···N). One obvious result of this packing is a much lower melting point of −56.2 °C [4] compared with that of 5.49 °C for benzene [5].

To find the reason for the different packing modes, the lattice energies of benzene, borazine, and borazine in the low-pressure benzene lattice have been calculated, applying a slightly modified version of an approach published recently [9].

2. Computational Methods

As described in two previous papers [9, 10], the lattice energy (ΔE_{lat}) has been approximated as the sum of the dispersion- (ΔE_{dis}), the electrostatic- (ΔE_{els}), the induction- (ΔE_{ind}), and the (closed shell) repulsion energy (ΔE_{rep}):

$$\Delta E_{\text{lat}} = \Delta E_{\text{dis}} + \Delta E_{\text{els}} + \Delta E_{\text{ind}} + \Delta E_{\text{rep}}. \tag{1}$$

To calculate the components of the lattice energy, common approximate expressions have been used in this paper which are derived from perturbation theory introducing in part severe approximations (e. g., [11–15]). The electrostatic contribution to the lattice energy is approximated by a point charge (Coulomb) model

$$\Delta E_{\text{els}} = \frac{1}{2} K_{\text{c}} \sum_{\text{a}\in\text{A}} \sum_{\text{b}\in\text{B}\neq\text{A}} q_{\text{a}} q_{\text{b}} r_{\text{ab}}^{-1}. \tag{2}$$

Here the first summation runs over all atoms a of the reference molecule (A), and the second one covers the atoms b of all other molecules (B≠A) of the lattice. q_{a} and q_{b} are the (Mulliken) charges of atoms a and b, calculated using the corresponding semiempirical wave function of the isolated molecule, while r_{ab} is their interatomic distance. Here, like in the calculation of the other components, the coordinates used for A can, for example, be those of the experimentally determined connected set transformed to a cartesian coordinate system. The coordinates of the molecules B are obtained from those of the connected set by application of the corresponding space group and translational symmetry. In cases where calculated molecular structures are used to obtain lattice energies, the coordinates of A and B are obtained by a rigid fit of the calculated atomic coordinates to the experimentally determined positions.

If charges and interatomic distances are used in atomic units, the constants K_{c} (627.5095 kcal mol^{-1} ·Hartree^{-1}) and 1/2 convert the energy from Hartrees (atomic energy units) per molecule to kcal/mol. Summation of the pairwise contributions to the electrostatic energy was performed employing the *Bertaut* method [16] in the version introduced by *Williams* [17–19] (“accelerated summation”), employing a separation constant $k = 0.3$ [17] and including direct as well as reciprocal space contributions.

Direct evaluation of the expression for the dispersion energy derived from perturbation theory is quite time-consuming since it requires huge extended basis sets including polarization and diffuse functions [20]. Significantly faster calculations, employing wave functions obtained with semiempirical methods based on the ZDO approximation and using a minum basis set, yield dispersion energies which are much too positive [20, 21]. Alternatively one might use either the London- or the Slater-Kirkwood formula at the atomic level which requires *atom-in-molecule* polarizabilities. In this paper the well-known London formula

$$\Delta E_{\text{dis}} = -\frac{1}{2} K_{\text{c}} \frac{3}{2} F_{\text{L}} \sum_{\text{a}\in\text{A}} \sum_{\text{b}\in\text{B}\neq\text{A}} \alpha_{\text{a}} \alpha_{\text{b}} r_{\text{ab}}^{-6}, \tag{3a}$$

$$F_{\text{L}} = [U_{\text{A}} U_{\text{B}} / (U_{\text{A}} + U_{\text{B}})] \tag{3b}$$

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[c] $E_{\text{dis}} = -3/4 \cdot I_{\text{A}} \alpha_{\text{A}}{}^2 \cdot R^{-6} = -C_6 \cdot R^{-6}$, where R is the intermolecular distance, I_{A} the ionization potential of molecule A, and α_{A} its polarizability.

has been used to calculate the dispersion contribution to the lattice energy, where U_{A} and U_{B} are *twice* [22–26] the vertical molecular ionization potentials of the interacting molecules approximated by the calculated energies (HF/6-31+G*) of their highest occupied molecular orbitals ($\varepsilon_{\mathrm{HOMO}}$, Koopmans' theorem [27]), while α_{a} and α_{b} are atom-in-molecule polarizabilities obtained as described in the appendix. In all cases considered in this paper the molecules A and B belong to the same species and, therefore, $F_{\mathrm{L}} = {}^1\!/_2 U_{\mathrm{A}}$.

Since no atomic polarizability tensors are available (see Appendix), (4) has been used to calculate the induction energy:

$$\Delta E_{\mathrm{ind}} = -\frac{1}{2} K_{\mathrm{c}} \sum_{\mathrm{a} \in \mathrm{A}} [\alpha_{\mathrm{a}} |\boldsymbol{E}_{\mathrm{a}}|^2]. \tag{4}$$

This expression differs from formula (5) used in [9] in that in the present study α_{a} is the scalar polarizability of atom a, while the polarizability tensor $\boldsymbol{\alpha}_{\mathrm{a}}$ is used in (5). $\boldsymbol{E}_{\mathrm{a}}$ is the total electric field at the position of atom a caused by all atoms not belonging to A

$$\Delta E_{\mathrm{ind}} = -\frac{1}{2} K_{\mathrm{c}} \sum_{\mathrm{a} \in \mathrm{A}} [\boldsymbol{E}_{\mathrm{a}}^t \boldsymbol{\alpha}_{\mathrm{a}} \boldsymbol{E}_{\mathrm{a}}]. \tag{5}$$

Destabilizing contributions to the lattice energy due to closed shell repulsion ("steric effects") were calculated employing an approximate expression for the exchange repulsion energy [28]:

$$\Delta E_{\mathrm{rep}} = K_{\mathrm{c}} \tau \sum_{\mathrm{B} \neq \mathrm{A}} \sum_{\mathrm{k} \in \mathrm{A}} \sum_{\mathrm{l} \in \mathrm{B} \neq \mathrm{A}} \left[\sum_{\mathrm{p} \in \mathrm{a}} \sum_{\mathrm{q} \in \mathrm{b}} c_{\mathrm{kp}} c_{\mathrm{lq}} S_{\mathrm{pq}} (r_{\mathrm{ab}}^{-1/2}) \right]^2 . \tag{6}$$

The indices k and l run over all occupied molecular orbitals of molecules A and B$\neq$A, calculated with one of the semiempirical methods. p and q refer to the corresponding atomic orbitals at atoms a and b with LCAO-MO-coefficients c_{kp} and c_{lq}, respectively ($p \in$ a, $q \in$ b). S_{pq} is their overlap integral and r_{ab} the distance between atoms a and b. In a strict sense, τ is not only a function of the interacting atoms but also of the interatomic distance [12, 28]. In many cases, however, it is approximated by a constant, sometimes even adjusted to fit the experimental results. Thus, Murrell et al. [12] used values of $\tau = 1.016$ and 1.319 for the interaction between two hydrogen and two carbon atoms. A value of 1.0 was used in this study. In the calculation of the repulsion energy only overlap integrals between valence shells were considered, and they were calculated employing Slater type orbitals and orbital exponents optimized for molecular calculations [29]. Different from some of the semiempirical methods, identical exponents were used for the $2s$ and $2p$ functions. Since the single contributions in square brackets decrease exponentially with the interatomic distance, accelerated summation is dispensable in this case and the sum was evaluated directly.

The selection of the molecular model for a calculation of the lattice energy is by no means a trivial task, since there is no *a priori* choice for the structure of a molecule in the solid state. In the previous studies [9, 10] the unchanged experimental values have been used. However, if the crystal structures of interest, like those used in this paper, have been determined under quite different conditions and, maybe, at significantly different levels of accuracy, normalization to a common standard is useful. Therefore, molecular geometries have been used which were optimized within the framework of the *Hartree-Fock* approximation, using the 6-31+G* basis set and the GAUSSIAN94 suite of quantum chemical routines [30]. The optimized molecular structures were then fitted to the experimentally determined positions [31] and the resulting coordinates have been used to generate the corresponding crystal lattices.

None of the analytical expressions used to calculate the lattice energies contains parameters which were adjusted to fit experimental lattice energies. As a result, the calculated lattice energies might be different from their experimentally determined counterparts, where such values are available. However, it is not the *absolute* value of the lattice energy that is of interest in this study, but rather the *difference* between such values.

3. Results and Discussion

The results of the semiempirical calculations are compiled in Table 1. For comparison the lattice energies calculated for the low-pressure modification of benzene are also listed. Compared with the experimental value for the heat of sublimation of benzene (10.5–11.1 kcal/mol [32]), these lattice energies are clearly too negative. It should be kept in mind, however, that using semiempirical methods it is not so much the aim to reproduce *absolute* values but rather to obtain accurate *relative* stabilities. All methods, except AM1, give somewhat more negative electrostatic energies for borazine than for benzene. Omitting

Table 1. Lattice energies and their components (in kcal/mol) of low pressure benzene and borazine in different lattices. Molecular geometries and ionization potentials have been calculated at the HF/6-31+G* level. benz/benz and boraz/boraz are the values for benzene and borazine in their own lattices, while boraz/benz refers to borazine in the low-pressure lattice of benzene.

Method	ΔE_{dis}	ΔE_{els}	ΔE_{ind}	ΔE_{rep}	ΔE_{lat}
CNDO/2 [42]					
benz/benz	−22.28	−0.01	0.00	+6.95	−15.34
boraz/boraz	−18.40	−0.39	−0.06	+8.20	−10.65
boraz/benz	−15.67	+0.40	−0.13	+6.52	−8.88
INDO [43]					
benz/benz	−22.28	−0.08	+0.02	+7.03	−15.35
boraz/boraz	−18.40	−0.39	−0.07	+8.27	−10.59
boraz/benz	−15.67	+0.50	−0.18	+6.59	−8.76
MINDO/3 [44]					
benz/benz	−22.28	−0.01	0.00	+6.89	−15.40
boraz/boraz	−18.40	−0.03	−0.04	+8.38	−10.09
boraz/benz	−15.67	+0.39	−0.10	+6.50	−8.88
MNDO [45]					
benz/benz	−22.28	−1.15	−0.26	+6.60	−17.09
boraz/boraz	−18.40	−1.64	−0.22	+7.44	−12.82
boraz/benz	−15.67	−1.31	−0.30	+5.89	−11.39
AM1 [46]					
benz/benz	−22.28	−4.54	−1.05	+6.29	−21.58
boraz/boraz	−18.40	−3.57	−0.87	+7.32	−15.52
boraz/benz	−15.67	−3.28	−0.65	+5.79	−13.81
MSINDO [47]					
benz/benz	−22.28	−0.11	−0.02	+6.81	−15.60
boraz/boraz	−18.40	−0.72	−0.08	+7.77	−11.43
boraz/benz	−15.67	−0.42	−0.15	+6.26	−9.14

Table 2. Energies of interaction (ΔE_{int}) between an arbitrarily chosen reference molecule and all those neighbours in the crystal lattice to which the shortest intermolecular distance does not exceed 3 Å (in kcal/mol). Molecular geometries have been calculated at the HF/6-31+G* level.

Mol./lat.	ΔE_{int} *HF*	ΔE_{int} *MP2*	ΔE_{cor} *MP2*	ΔE_{dis}
benz/benz	+3.8	−21.2	−25.0	−22.3
boraz/boraz	+3.4	−18.2	−21.6	−18.4
boraz/benz	+4.4	−10.2	−14.6	−15.7

the AM1 data, the average value of this difference is −0.36 kcal/mol. At the same time the repulsion energy increases on the average by 1.14 kcal/mol while the stabilizing contribution of the disperion energy is reduced by 3.88 kcal/mol. These effects add up to lattice energies which are on the average 4.88 kcal/mol less negative for borazine than for benzene. While this explains the much lower melting point of the title compound, further calculations are necessary to explain why this compound crystallizes in a lattice different from the typical “herringbone” packing of benzene. To find an answer to this question, the lattice energy of borazine in the low pressure benzene lattice was calculated. When borazine in its HF/6-31+G* structure is transferred to the benzene lattice, the shortest intermolecular distance is 2.318 Å, while it is 2.533 Å in the crystal lattice of its own. To obtain a value of the lattice energy which is comparable to the one calculated for the title compound in its own lattice, the lattice constants ***a***, ***b*** and ***c*** were isotropically increased by 3.8%, resulting in values which give a shortest intermolecular distance of 2.53 Å. For this hypothetical lattice the electrostatic and dispersion energy are more positive by about 0.50 and 2.73 kcal/mol than for borazine in its own lattice. Although at the same time the repulsion energy is in the average reduced by 1.64 kcal/mol, this is not sufficient to compensate for the loss of stabilizing energy, especially caused by an unfavourable increase of the dispersion energy.

To obtain an independent support for the semiempirically calculated order of lattice energies, the energy of interaction between an arbitrarily chosen reference molecule and all neighbouring molecules up to a shortest intermolecular distance of 3 Å has been computed at the *ab initio* level. Pairwise additivity has been assumed in these calculations. The energies of interaction calculated at the HF level can roughly be compared with the sum of ΔE_{els}, ΔE_{ind}, and ΔE_{rep}. For all three structures these values are positive, indicating that the sum of electrostatic and induction energy is not sufficient to stabilize these lattice fragments. Working at the MP2 level [33] an energy of interaction of −18.2 kcal/mol was obtained for borazine in its own lattice (Table 2). At −10.2 kcal/mol the corresponding energy is much more positive for borazine in the lattice of the low pressure modification of benzene. Since no correction for the basis set superposition error has been applied, the MP2 values are most likely too negative. However, it is unlikely that such a correction will change the order of stability. Thus it has convincingly been shown that the interaction of a borazine molecule with its neighbours is less favourable in the benzene lattice than in the crystal lattice of its own.

4. Appendix

In the case of open-chain molecules *atom-in-molecule* polarizabilities can be calculated by *Metzger’s* combination of the MINDO/3-FP method and a partitioning of the molecular dipole moment [34]. However in the case of cyclic molecules like those which are of interest in this paper, this method can only be applied if the sum of the charges of the ring atoms is zero [34]. This is clearly not the case for the molecules under consideration. Therefore another method was used to obtain *atom-in-molecule* polarizabilities for both compounds. In the case of benzene it was assumed that $\alpha_{\mathrm{mol}} = 6\alpha_{\mathrm{C}} + 6\alpha_{\mathrm{H}}$. Employing the frequently used value for the polarizability of hydrogen of 0.42 Å^3 [35, 36] together with the experimental molecular polarizability (*v.s.* $\alpha_{\mathrm{mol}} = 10.38$ Å^3) a value of $\alpha_{\mathrm{C}} = 1.31$ Å^3 has been obtained for the polarizabilty of the aromatic carbon atoms. Things are not so easy in the case of borazine. One of the fundamental assumptions of organic chemistry is that the properties of an atom in a molecule change *gradually but not in principle* with its individual chemical environment (see for example [37]). Based on this consideration, the polarizability α_{a} of an atom a in a molecule might be expanded as

$$\alpha_{\mathrm{a}} = \alpha_{0,\mathrm{a}} + \delta, \tag{7}$$

where $\alpha_{0,\mathrm{a}}$ is a basic value for atom a, and δ takes into account the influence of its particular chemical environment in the molecule under consideration. Keeping in mind the interpretation of the polarizability of an atom as the mobility of its electrons, it is reasonable to assume that α_{a} does not only increase with decreasing electronegativity (χ_{a}) of the atom itself but also with that of its next neighbours. Therefore, the polarizability of a nitrogen-based hydrogen atom ($\mathrm{H_N}$) is expected to be lower than that of an H atom bonded to boron ($\mathrm{H_B}$). This assumption is supported by the results of MINDO/3-FP [34] calculations on the HF/6-31+G*-optimized structures of H_2B-NH_2 and H_2B-NH-BH_2[d]. According to these calculations the *atom-in-molecule* polarizability of the hydrogen atoms bonded to boron is about 1.3 times higher than that of the nitrogen-based hydrogens. For $\alpha_{0,\mathrm{H}}$ a value of 0.42 Å^3 was chosen, which is the polarizability of an H atom in a CH_2 group [35]. The same value is also frequently used for hydrogen atoms in a variety of organic compounds [36]. Since on the most commonly used electronegativity scales [38 – 41] χ_{C} is close to the average value of χ_{B} and χ_{N}, it was assumed that the polarizability of a carbon-based hydrogen atom is also about halfways between those of an N- and a B-based hydrogen. Therefore, the approximate relationship

$$\alpha'_{\mathrm{H_B}}/\alpha'_{\mathrm{H_N}} \approx (0.42+\delta)/(0.42-\delta) = 1.3 \tag{8}$$

was employed, resulting in $\alpha'_{\mathrm{H_B}} = 0.475$ Å^3 and $\alpha'_{\mathrm{H_N}} = 0.365$ Å^3, respectively. Using the empirically corrected[e] *ab initio* molecular polarizabilities of H_2B-NH_2 and H_2B-NH-BH_2 (3.513 and 5.376 Å^3) and a similar equation as in the case of benzene:

$$m\alpha'_{\mathrm{H_N}} + n\alpha'_{\mathrm{H_B}} + p\alpha'_{\mathrm{N}} + q\alpha'_{\mathrm{B}} = \alpha(H_{m+n}B_qN_p), \tag{9}$$

polarizabilities of $\alpha'_{\mathrm{B}} = 1.278$ Å^3 and $\alpha'_{\mathrm{N}} = 0.555$ Å^3 were obtained. These polarizabilities of $\mathrm{H_B}$, $\mathrm{H_N}$, B, and N have then been used as starting values in a least-squares refinement to reproduce the polarizabilities of H_2B-NH_2, H_2B-NH-BH_2, and $B_3N_3H_6$, resulting in the final values $\alpha_{\mathrm{B}} = 1.304$ Å^3, $\alpha_{\mathrm{N}} = 0.581$ Å^3, $\alpha_{\mathrm{H_B}} = 0.512$ Å^3, and $\alpha_{\mathrm{H_N}} = 0.402$ Å^3. These values for the atomic polarizabilities were employed in all subsequent calculations of the lattice energy.

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[d] The molecules were constrained to planarity in the optimization process. $E_{\mathrm{tot}}(\mathrm{H_2BNH_2}) = -81.493801$ a. u., $E_{\mathrm{tot}}(\mathrm{H_2BNHBH_2}) = -106.784168$ a. u.

[e] Comparison of experimental (α_{exp}) and calculated polarizabilities (α_{cal}; HF/6-31+G*) of benzene and borazine led to the relation $\alpha_{\mathrm{exp}} \approx 1.15\alpha_{\mathrm{cal}}$.

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