

temperature of 1.07 K at both ambient pressure and a pressure of 5 kbar. Further experiments using rf penetration depth measurements⁴ showed no evidence of superconductivity at ambient pressure down to a temperature of ~ 0.45 K. We cannot rule out a possible superconducting transition at $T > 4$ K and under applied pressure.

Thus, contrary to the (TMTSF)₂X systems in which anion disorder/order transitions appear to cause metal/insulator transitions, the β -(ET)₂X synthetic metals may remain metallic to the lowest temperatures regardless of anion disorder.

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Note Added in Proof. As a further test of the effect of molecular and anionic order on superconducting transitions in β -(ET)₂X salts, we have synthesized β -(ET)₂(I-Au-I). The unit cell volume is 845.2 Å³, compared to 842.3 Å³ for β -(ET)₂I₂Br reported herein; however, the AuI₂⁻ derivative is completely ordered. It also has the highest ambient-pressure superconducting transition temperature (onset $T_c \approx 5$ K, rf penetration depth measurements) reported for any organic conductor.

Registry No. ET, 66946-48-3; (ET)₂I₂Br, 96164-65-7; (*n*-Bu₄N)I₂Br, 3419-99-6; (*n*-Bu₄N)Br, 1643-19-2; I₂, 7553-56-2.

Supplementary Material Available: Tables of crystal structure data collection and refinement parameters (Table X1) and final atom positional and anisotropic temperature factors (Table X2) and a figure showing the S-atom labeling scheme for the ET molecule (Figure X1) (3 pages). Ordering information is given on any current masthead page.

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Articles

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Theoretical Studies on N-Bonded Pyrazole Derivatives of Boron

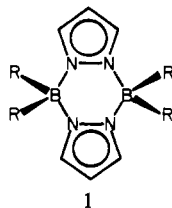
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CNDO calculations on the sequential processes (1) $R_2BH + Hpz \rightarrow R_2Bpz + H_2$ and (2) $2R_2Bpz \rightarrow R_2B(\mu-Pz)_2BR_2$ (where $pz = \text{pyrazolyl} = N_2C_3H_3$) indicate that for $R = H$ both steps are energetically favorable, particularly the dimerization (2). In addition, the latter also leads to electronic saturation of the boron atom, and the energy of the resultant pyrazole is independent of the conformation of the molecule. For $R = \frac{1}{2} CH_3N(CH_2)_2NCH_3$, only step 1 yielding the monomer is exothermic, whereas step 2 is greatly dependent on the geometry of the central B_2N_4 ring (in addition to provoking a considerable charge increase on the boron atom). Another process, i.e., (3) $R_2Bpz + Hpz \rightarrow R_2B(\mu-pz)_2H$, is exothermic in both cases, but for $R = H$ the pyrazole formation (2) is much more strongly favored. The theoretical data are in good agreement with experimental results.

Introduction

When a trigonal borane, BR_3 , is reacted with pyrazole, Hpz , or a C-substituted derivative thereof in a 1:1 molar ratio, ready condensation occurs to yield a transient pyrazol-1-ylborane, R_2Bpz . As a rule, the latter species immediately dimerizes to form a pyrazole of the general structure 1.¹



The pyrazoles, $R_2B(\mu-pz)_2BR_2$, have been found to be chemically extremely stable. For example, they are generally unaffected by air or water, and various organic transformations

have been accomplished at the carbon sites of the bridging pyrazole groups without destruction of the central B_2N_4 ring.² This stability has been rationalized in terms of steric as well as electronic factors.¹ However, some monomeric pyrazol-1-ylboranes, i.e., symmetrical cleavage products of pyrazoles, have recently become available.³⁻⁷ Experimental data appear to indicate that monomeric pyrazol-1-ylboranes exist only when the boron atom is simultaneously bonded not only to a pyrazolyl group but also to strongly electron-donating substituents. In order to better understand these observations and the general electronic and steric features of pyrazole derivatives of boron, several semiempirical studies have been performed on these species.

Experimental Section

The method chosen was the CNDO (complete neglect of differential overlap) molecular orbital approach of Pople and co-workers.⁸ This

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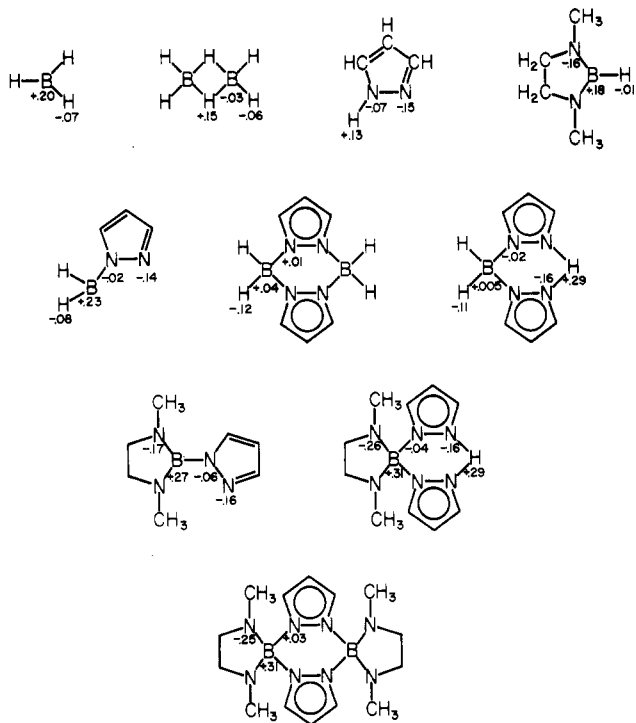


Figure 1. Selected calculated atomic charges for some molecules of interest.

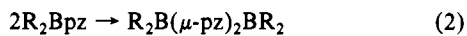
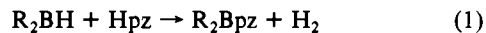
method was considered preferable to other semiempirical approaches such as EHMO (extended Hückel molecular orbital) methods because of its explicit inclusion of nuclear repulsion terms. All calculations were carried out on an IBM 3083 computer with the program CNINDO-DYNAM⁹ an expandable and more efficient version of the original CNINDO program.¹⁰ The CNDO/2 parameters suggested by Pople and co-workers⁸ were unchanged.

Total energies were computed for all species with smoothed experimental geometries.^{11,12} Reaction energies were taken as the computed total energy of all products minus the computed total energy of all reactants. Although, as expected, the energy changes computed with the CNDO method are much too large in absolute value, it is their relative magnitudes that are significant in the following discussion.

Some calculated atomic charges of various species of interest in the present study are given in Figure 1.

Results and Discussion

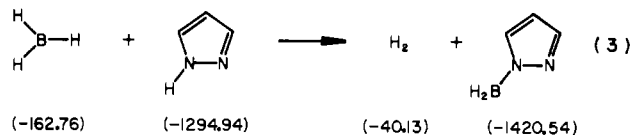
The only known cases where pyrazol-1-ylboranes exist as isolable monomers, R_2Bpz , are those where $R + R = NCH_3$ or $(CH_2)_nNCH_3$ [$n = 2, 3$], i.e., where boron is incorporated into a cyclic system and bonded to strongly electron-donating nitrogen atoms; all other species exist as the dimeric pyrazaboles, **1**. In search of an explanation of these reaction preferences, calculations on the energetics of the following reaction sequences were undertaken:



In all cases studied, changes in the charge on the boron atom, q_B ,

measured in units of the electron charge, were examined. According to valence saturation arguments, favored reactions of boron are those in which the electron deficiency of the boron atom is removed, such that q_B approaches zero.

The first reaction considered was that of borane(3) with pyrazole (eq 3). CNDO-computed total energies in eV are listed

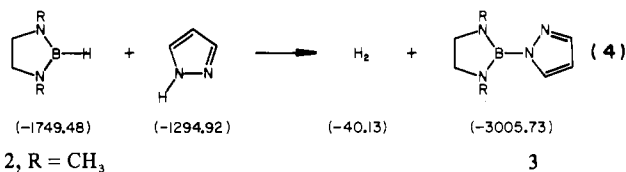


below each species. The energy change ($\Delta E = -2.99$ eV) was found to be small though favorable for formation of H_2Bpz . The charge on the boron atom indicates that the electron deficiency on boron in BH_3 ($q_B = 0.20+$) is not removed in the resultant H_2Bpz species but rather increases slightly, such that $q_B = 0.23+$. Dimerization of H_2Bpz according to eq 2 to yield the parent pyrazabole, i.e., $2H_2Bpz \rightarrow H_2B(\mu\text{-pz})_2BH_2$, is highly favorable with a reaction energy change ΔE of -16.82 eV. In addition, the charge on the boron atoms in the pyrazole is reduced to $0.04+$, indicating that the boron atom valence is quite saturated.

The energy of the parent pyrazabole was found to be quite insensitive to the specific conformation of the central B_2N_4 ring and also to the relative arrangement of the two pyrazole rings. For example, with smoothed X-ray data for pyrazabole¹² (B_2N_4 ring in boat conformation with the two pyrazole rings pointing downward in a butterfly arrangement), the total energy was found to be -2857.90 eV. For a significantly different structure in which a *planar* B_2N_4 ring is coplanar with the two pyrazole rings, the total energy was -2857.79 eV. Both boat and chair conformations of the B_2N_4 ring with the two pyrazole rings coplanar with the N_4 plane have identical total energies, -2857.84 eV. The essentially identical energies of all these species indicate that, in the dimerization process, the relative tilt angle of two approaching H_2Bpz moieties is not critical for successful dimerization.

In conclusion, both valence saturation arguments and energy considerations favor the dimerization of H_2Bpz to yield pyrazabole, $H_2B(\mu\text{-pz})_2BH_2$.

In a similar study on the reaction of 1,3-dimethyl-1,3,2-diazaboracyclopentane (**2**) with Hpz according to eq 4, the charge

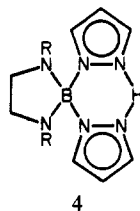


on the boron atom in **2** ($q_B = 0.18+$) was found to increase to $0.27+$ in the product **3**. The reaction is predicted to be exothermic with $\Delta E = -1.99$ eV.

Dimerization of **3** to yield a pyrazabole in accordance with eq 2 is, however, energetically unfavorable with $\Delta E = +2.47$ eV for the boat form of the resultant central B_2N_4 ring. In the boat form of this dimer, hydrogen atoms on the two methyl groups may approach each other to a vicinity of 0.5 Å. If the B_2N_4 ring is made planar, the total energy of the dimer is lowered by 12.08 eV, indicating that, unlike the case of the previously discussed dimer $H_2B(\mu\text{-pz})_2BH_2$, this particular pyrazabole would be extremely sensitive to the conformation of the B_2N_4 ring. The sharp and deep potential well associated with the conformation of this ring suggests that only a very few restricted orientations of two monomeric molecules, **3**, would succeed in bond formation, i.e., generation of a pyrazabole. Moreover, the charge on the boron atom for a pyrazabole derived from **3** with boat conformation is $q_B = 0.31+$, increasing to $q_B = 0.32+$ for a pyrazabole with a planar B_2N_4 ring.

In order to determine the extent to which repulsion in the boat-form dimer of **3** may be due to methyl-methyl or methyl-pyrazolyl group interactions, the planar dimer of **3** was dissected by removing a boron moiety and replacing it with a hydrogen atom, to give a structure **4**. The energy of the species **4**, with a planar

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conformation of the BN_4H ring:
 planar, $E = -4302.84 \text{ eV}$
 boat, $E = -4302.64 \text{ eV}$

BN_4H ring, was found to be only 0.20 eV below that of the corresponding boat form. This result suggests that most of the repulsion in the dimer is due to methyl–methyl interaction, which is minimized in planar and chair forms of the dimer. Thus, a very specific geometry is required for the formation of a pyrazabole-type dimer of 3.

Subsequent removal of Hpz from the molecule 4 with a planar BN_4H ring yielded the distorted form of the monomer 3 necessary to form the dimer with a planar B_2N_4 ring. The energy of this monomer was about 2 eV above that of the monomer in its normal geometry, indicating that the conformation needed by the monomer to form the pyrazabole requires considerable excitation energy.

Thus, the dimerization reaction sequence (2) with 3 as the reactant is predicted to be unlikely by both energy considerations and valence saturation arguments.

Another process examined in this study involves the interaction of the monomeric pyrazol-1-ylborane 3 with pyrazole according to eq 5. This latter process could potentially compete with the



dimerization of 3. Indeed, calculations show that the reaction of H_2Bpz with Hpz is exothermic with $\Delta E = -4.02 \text{ eV}$. Furthermore, the charge on the boron atom is reduced to $q_{\text{B}} = 0.005+$ upon formation of this adduct. The resultant hydrogen bridge appears to be a normal although bent hydrogen bond with a small charge, $q_{\text{H}} = 0.29+$, developed on the hydrogen atom. Although energetics and valence saturation arguments indicate that this adduct should be stable, the dimerization reaction (2) is much more strongly favored by the larger energy change.

On the other hand, when 3 was reacted with Hpz, adduct formation was indeed observed experimentally.^{4,6,7} The present calculations indicate that this process is slightly exothermic with $\Delta E = -1.99 \text{ eV}$, although the charge on B increases from $q_{\text{B}} = 0.27+$ in 3 to $q_{\text{B}} = 0.30+$ in 4. Thus, in this latter case, energy considerations favor the formation of the adduct rather than the dimerization process by 4.46 eV.

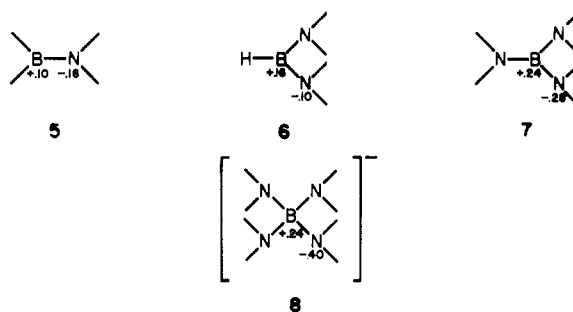
Conclusions

The present calculations indicate that in the dimerization of H_2Bpz to yield pyrazabole the energetics of the process are quite

favorable and that no specific geometry of the dimer is more favored than others. The charge on the boron atom in pyrazabole, 0.04+, indicates almost complete electron saturation of the boron atom.

In contrast, formation of the dimer $\text{R}_2\text{B}(\mu\text{-pz})_2\text{BR}_2$ with $\text{R} = \frac{1}{2} \text{CH}_3\text{N}(\text{CH}_2)_2\text{NCH}_3$ is energetically favorable only for those very specific geometries in which methyl–methyl interactions are avoided. Furthermore, with this R the valence saturation of the boron atom in reaction sequences 1 and 2 progressively worsens; q_{B} in R_2BH (where boron is bonded to two N atoms) is 0.18+, increasing to 0.27+ in R_2Bpz (in which boron is bonded to three N atoms) and then to 0.31+ in the dimer (in which boron is bonded to four N atoms). This result conflicts with the general assumption that an increase in the number of N atoms coordinated to boron increases its electronic saturation.

As a test of this fundamental principle, calculations on the four small molecules 5–8 were performed, with geometries of the first



three derived from those of corresponding (dimethylamino)boranes,^{13,14} with the exception that unlike the true tris(dimethylamino)borane structure, which has out-of-plane methyl groups, structure 7 was taken as planar. In a planar structure the electron-donating potential of the nitrogen atoms should be a maximum. The charges computed for the boron and nitrogen atoms in the various structures, especially when compared with that of the highly saturated boron atom in diborane(6) [for which $q_{\text{B}} = -0.03$], indicate that increasing the number of nitrogen atoms coordinated to a boron atom does not increase its saturation.

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Registry No. 1 (R = H), 16998-91-7; 1 (R₂ = $\text{CH}_3\text{N}(\text{CH}_2)_2\text{NCH}_3$), 96129-04-3; Hpz, 288-13-1; BH_3 , 13283-31-3; $(\text{CH}_3\text{N}(\text{CH}_2)_2\text{NCH}_3)\text{BH}$, 38151-26-7.

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