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AB INITIO ELECTRONIC STRUCTURE CALCULATIONS OF THE C_2H_5B POTENTIAL ENERGY SURFACE: THE STABILITY OF BORIRANE

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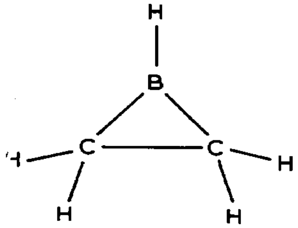
Summary

The optimum geometries and relative energies of the five most probable isomers of formula C_2H_5B are calculated using ab initio SCF theory and fourth-order perturbation theory. Results indicate that contrary to the isoelectronic cyclopropyl cation–allyl cation system, the open-ring, planar form of C_2H_5B is 102.4 kJ/mol higher in energy than the closed-ring form. Interconversion pathways are investigated and lower bounds to the activation energies are determined. It is concluded that the closed ring form is a stable minimum on the C_2H_5B potential surface.

Introduction

Until 1983 there was only indirect evidence that derivatives of I (borirane) might exist [1–3]. With the reports of Berndt et al. [4,5] of the synthesis of **A** and **B** comes increased interest in the stability of borirane.

In the present study we address the following three questions: (i) Which of the five most probable structural isomers of C_2H_5B, I–V is the lowest in energy?; (ii) If



(I)

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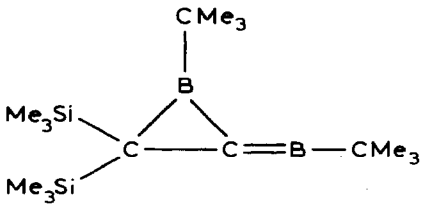
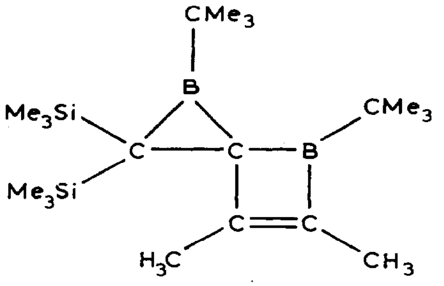
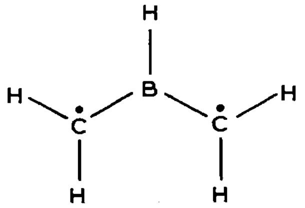


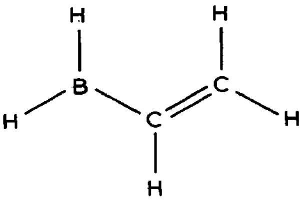
(A)



(B)



(II-S,T)



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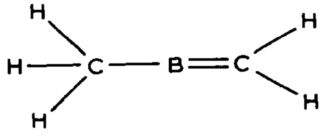

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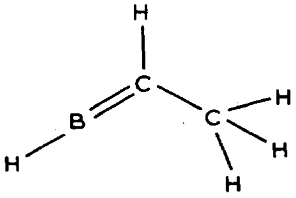


(V)

there are isomers of lower energy than I, can the pathways between such isomers and structure I be determined?; (iii) Do significant barriers to such interconversions exist? Note that isomer II is particularly interesting both because it represents the product of symmetry allowed disrotatory ring opening, and because it could exist as either a singlet or a triplet ground state.

Aside from theoretical interest in these molecules, owing in part to their small size and boron's conspicuous absence from those elements already incorporated into heteroatom cyclopropanes, there is also interest in substituted boriranes as useful synthetic intermediates for the organic chemist. Through utilization of already well characterized reagents and reactions, the boriranes suggest the opportunity of simultaneously or sequentially functionalizing adjacent carbon atoms in organic molecules with controlled stereochemistry. In delineating, by quantum mechanical methods, some of the chemistry of borirane experimental guidelines are provided for synthetic efforts.

Equilibrium geometries for structures I–V were obtained and subsequent energy calculations were performed to determine best estimates as to the relative energies of the five isomers. Finally, limited attempts to determine interconversion pathways among the various isomers (I–V) were made. The results are presented as well as their implications regarding the inherent stability of the cyclic structure I.

We call attention to the fact that for the purposes of this study we did not consider the likely possibility that the parent borirane would form a boron hydride dimer. The dimer itself could readily rearrange to products such as 1,6-boracyclohexane.

Methods

All ab initio molecular orbital calculations were carried out on the Quantum Theory Project's DEC VAX 11/780 computer using the Gaussian 82 series of programs [6]. The geometry optimization code was modified to use the Hessian update procedure of Head and Zerner [7].

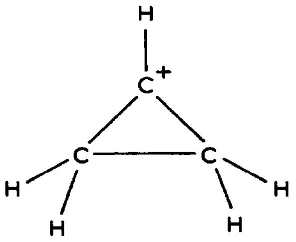
Calculations at the SCF level were of the restricted type for all closed shell systems and of the unrestricted type for the triplet structure, II(T). Initial geometries were determined via a semi-empirical INDO program [8] and then systematically refined via ab initio molecular orbital theory using first STO-3G and then 3-21 G basis sets as advocated by Pople [9–12]. At the optimized 3-21G basis set geometries energies were obtained through fourth order Rayleigh-Schrødinger, Møller-Plesset perturbation theory calculations employing the larger 6-31G** basis set.

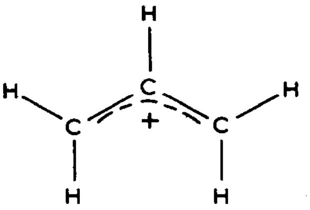
Molecular geometries were optimized completely, allowing all parameters to vary without regard to molecular symmetry. All structures were optimized successfully.

Results and discussion

$C_3H_5^+$

Initial calculations were to closely parallel previous work concerning the analogous and isoelectronic system composed of the cyclopropyl cation (VI) and the allyl cation (VII). In this case evidence indicates that the higher energy (151.8 kJ/mol) cyclopropyl cation VI undergoes a ring opening to the allyl cation VII via a disrotatory motion of the methylene groups with little or no activation energy required (Fig. 1).


(VI)


(VII)

After performing our own calculations on this system, it was found that a small barrier (0.08 kcal/mol) existed at the SCF/3-21G level. However, after the inclusion of correlation, this barrier was no longer present. Our results are summarized in Table 1 and are similar to those obtained by previous investigators [13,14].

C_2H_5B

The energies and optimized geometries of each of the five C_2H_5B isomers are

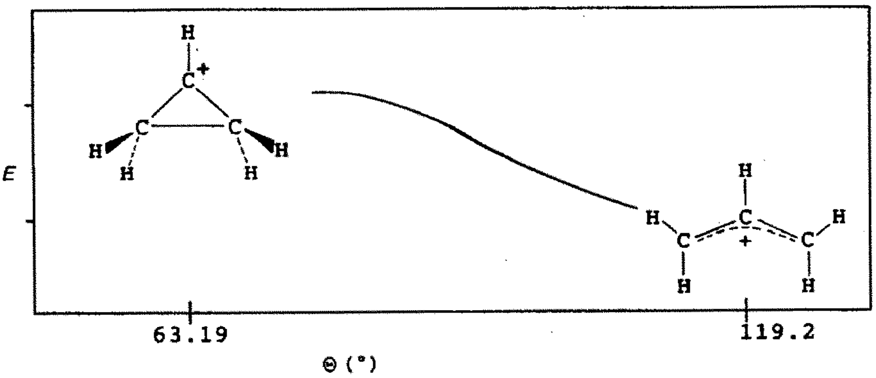


Fig. 1. $C_3H_5^+$ energy schematic as a function of the ring-opening angle, Θ.

given in Table 2 and Fig. 3, respectively. The relative energies of structures I, II-S, and III reported here are in good agreement with those reported by Budzelaar et al. [15]. However, while their work reported structure IV to be 7.6 kcal/mol above structure I, we found it to be 7.8 kcal/mol (32.6 kJ/mol) lower in energy than I. Additionally, we found structure V, not considered in Budzelaar et al., to have an energy lower than two of the structures they did consider.

Note that the relative energies of structures I and II are reversed from the positions calculated for the $C_3H_5^+$ analogues. The closed-ring structure I is lower in energy by 102.4 kJ/mol than the open-ring structure II. This result, though surprising at first, can be more readily understood in terms of the molecular orbital diagrams (Fig. 2, A–D) obtained from semi-empirical localized orbital calculations [16].

For the cyclopropyl cation the two most stable valence molecular orbitals (Fig. 2A) are the degenerate C–C σ bonds formed between the apical carbon of the ring and each of the two methylene carbons. Somewhat above these two orbitals lies the methylene–carbon to methylene–carbon σ bonding orbital. Transition to the allyl cation breaks only the weaker of the three C–C σ bonds, leaving the two more stabilizing bonding orbitals intact. The resulting planar structure of the allyl cation

TABLE 1

CALCULATED ENERGIES (hartrees) FOR $C_3H_5^+$ AS A FUNCTION OF THE RING-OPENING ANGLE, Θ (°)

Θ	SCF/3-21G	SCF/6-31G	MP2/6-31G**	MP4/6-31G**
63.19	−115.4670472	−116.1414378	−116.5208071	−116.5573614
70.77	−115.4662772	−116.1414001	−116.5252467	−116.5608165
73.00	−115.4664247			
83.00	−115.4775574			
93.00	−115.5004070			
103.00	−115.5255688			
113.00	−115.5499888			
119.24	−115.5421362	−116.2019832	−116.5803128	−116.6151787
130.00	−115.5369123			

TABLE 2

CALCULATED ENERGIES FOR STRUCTURES I–V

Structure	SCF/STO-3G		SCF/3-21G	
	Total (Hartrees)	Relative (kJ/mol)	Total (Hartrees)	Relative (kJ/mol)
I	−102.0193	00.00	−102.6870	00.00
II-S	−101.9325	+227.9	−102.6447	+111.0
II-T	−101.9948	+64.31	−102.6792	+20.46
III	−102.0268	−19.71	−102.7146	−72.47
IV	−102.0105	+23.10	−102.7142	−71.42
V	−101.9914	+73.26	−102.6846	+06.32

Structure	SCF/6-31G**		MP2/6-31G**	
	Total (Hartrees)	Relative (kJ/mol)	Total (Hartrees)	Relative (kJ/mol)
I	−103.2707	00.00	−103.6310	00.00
II-S	−103.2162	+143.1	−103.5896	+108.7
II-T	−103.2584	+32.30	−103.5687	+163.6
III	−103.2969	−68.78	−103.6503	−50.67
IV	−103.2838	−34.39	−103.6413	−27.03
V	−103.2600	+28.09	−103.6186	+32.56

Structure	MP4/6-31G**	
	Total (Hartrees)	Relative (kJ/mol)
I	−103.6659	00.00
II-S	−103.6269	+102.4
II-T	−103.6127	+139.7
III	−103.6877	−57.20
IV	−103.6783	−32.55
V	−103.6558	+26.52

gives rise to a π bonding orbital (Fig. 2B) delocalized among the three carbon centers which lends additional stability to the allyl cation relative to the cyclopropyl cation.

Conversely, the lowest energy molecular orbital in structure I is the methylene–carbon to methylene–carbon σ bonding orbital (Fig. 2C). The two apical-boron to methylene-carbon σ bonding orbitals are not the predominant stabilizing factors that the analogous C–C bonds are in the cyclopropyl cation, presumably due to less efficient overlap of the boron and carbon σ orbitals. Thus, the transition from structure I to structure II requires the breaking of the most stable bond in structure I.

Also, we note that the π bonding orbital (Fig. 2D) of structure II is not as stabilizing as the analogous orbital in the allyl cation due to less effective π orbital interaction among the boron and two carbons relative to the π interaction among the three carbons of the allyl cation. Thus, the formation of the π system does not compensate for the loss of the C–C bond as effectively for structure II as it does in the case of the allyl cation.

Having found II to be higher in energy than I, we now look to structures III–V to

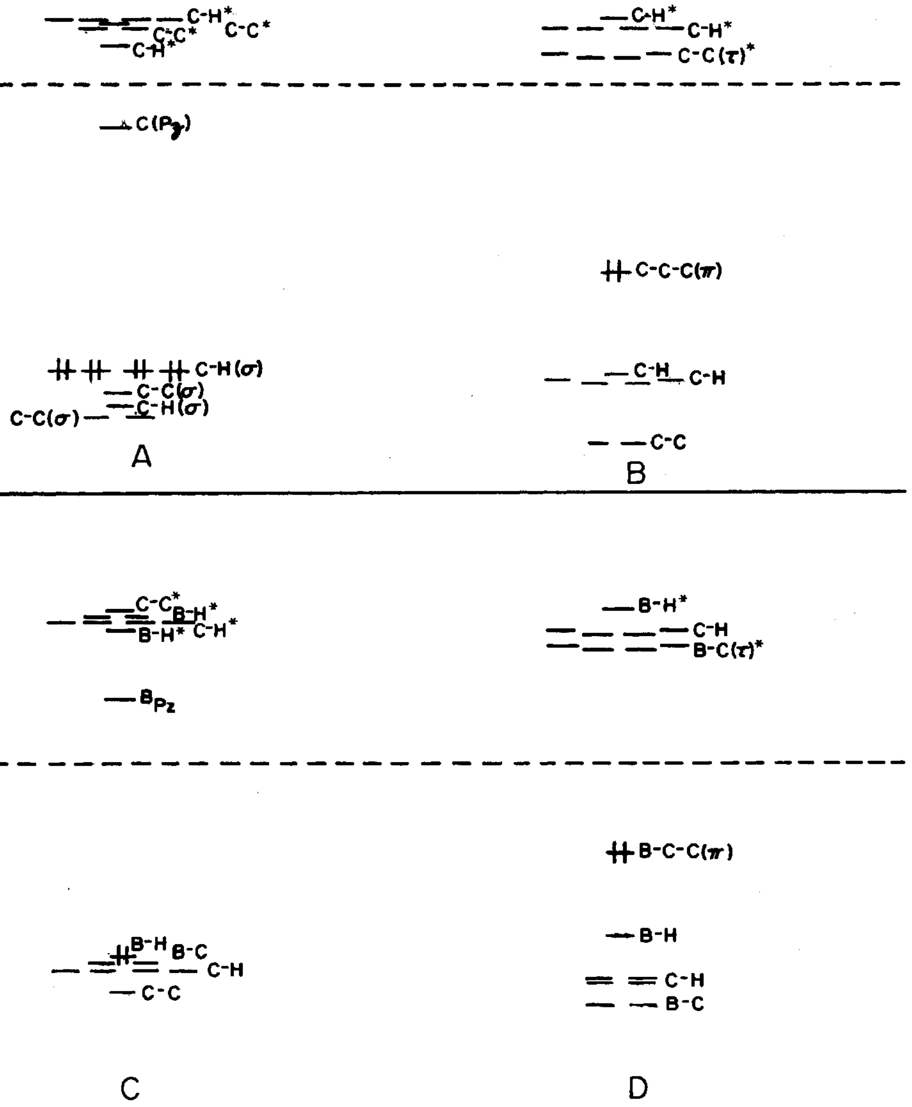
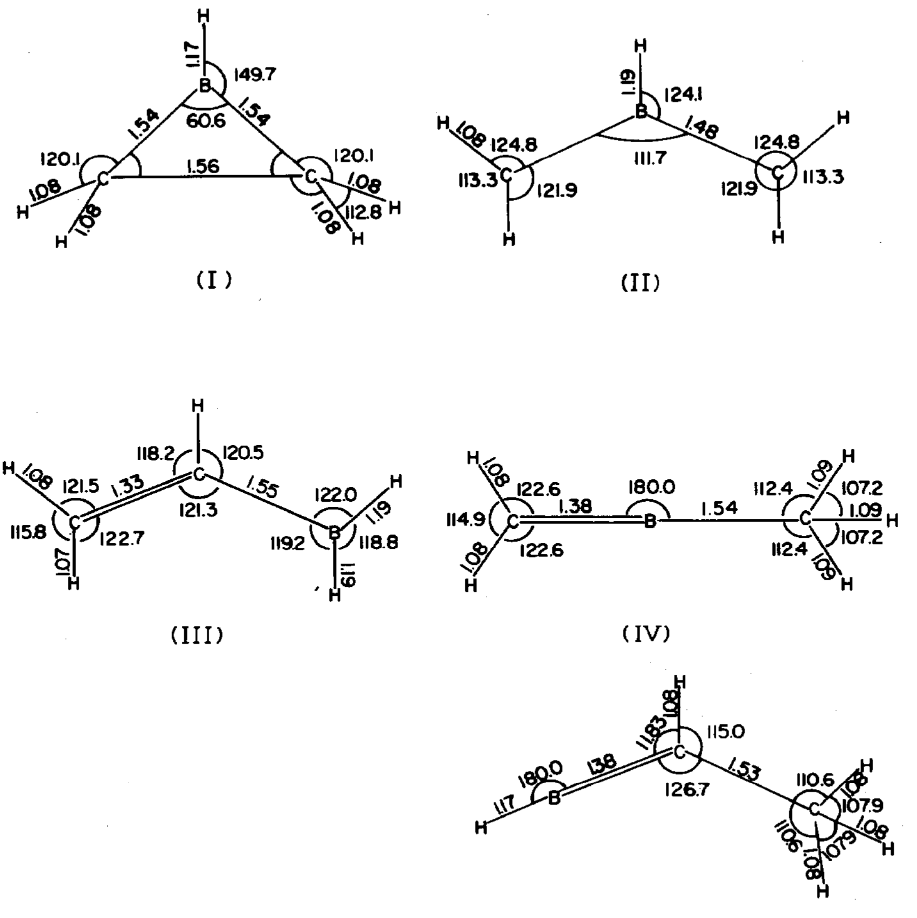


Fig. 2. Localized orbitals for the cyclopropyl cation, A; the allyl cation, B; borirane (structure I), C; and structure II (the open form), D. The highest occupied orbital is marked with two electrons.

find the most likely decomposition products of I. Of these remaining structures, III and IV lie the lowest in energy and would appear to be the leading candidates.

Structure I is essentially an equilateral triangle with the methylene hydrogens positioned such that it belongs to the C_{2v} point groups. Movement of the boron hydrogen out of the plane results in an increase in the SCF energy. This geometry is in close agreement with previous results [17] in which the molecule was constrained to the C_{2v} point group.

The optimized geometry of structure II, like its carbon analog, the allyl cation, is planar and belongs to the C_{2h} point group. Note that while all four C–H bond



(I) (II) (III) (IV) (V)

Fig. 3. Optimized structures at the 3-21G level.

lengths are the same, the four B–C–H bond angles are not. The C–B bond lengths at 1.48 Å, are between the single bond length of 1.54 Å (structures I, III, and IV) and the double bond length of 1.38 Å (structure IV), indicating some double bond character. However, this double bond character does not seem to be reflected in the stability of this structure relative to the cyclic structure, as discussed previously.

Among the five isomers studied, structure III proved to be the lowest in energy, presumably due to the stability of the vinylic functional group. The molecule is predicted to be planar, of C_s symmetry, with characteristic bond lengths and angles.

Structure IV has a linear C–B–C skeleton with a trigonal carbon on one end and an almost tetrahedral carbon on the other. The point group is C_s, there being a plane of symmetry which bisects the trigonal H–C–H angle as well as one of the tetrahedral H–C–H angles.

Finally, structure V is also of C_s symmetry, possessing one trigonal and one tetrahedral carbon. Bond lengths and angles are similar to those reported for structures I–IV.

TABLE 3

VIBRATIONAL FREQUENCIES FOR BORIRANE

Frequency (cm^{-1})	Symmetry
3356	B1
3277	A1
3269	A2
3205	B2
2867	A1
1787	A1
1536	B2
1535	A1
1506	B1
1394	A2
1295	B2
1194	A1
1067	B1
974	B2
810	A1
742	B2
579	B1
495	A2

It is worth observing that the preliminary and considerably less expensive INDO/1 geometry calculations did anticipate the magnitude of the relative stabilities of borirane I, dimethyleneborane II, and vinyl borane III. A correction term for the notorious tendency of INDO calculations to over estimate small ring stability was obtained from a reported experimental energy difference between the allyl and cyclopropyl cations [18]. Utilization of this correction term following INDO/1 calculations on the isoelectronic C_2H_5B series estimated borirane I, to be 83.7 kJ/mol lower in energy than II, and 167.4 kJ/mol higher than the vinyl borane (III) [19].

We report in Table 3 the predicted vibrational frequencies for structure I. These frequencies are estimated using the 3-21G basis set at the 3-21G optimized geometry. Such frequencies are usually too large and multiplication by a factor of about 0.90 usually gives good agreement with experiment.

Interconversion pathways

Interconversion pathways between I and its various isomers were investigated first at the SCF level and then with the inclusion of correlation. These pathways, with one exception, proved somewhat troublesome to determine and only limited success was achieved. Efforts were concentrated on the pathways between I and III, and I and IV, since III and IV were the lowest energy isomers among those studied.

The exception noted above is the pathway between structure I and structure II-S. Results indicate that I proceeds to II-S via a disrotatory ring opening, strictly analogous to the cyclopropyl cation ring opening except that now, the opening is an uphill process. Furthermore, the eigenvalues of the hessian matrix indicate that II-S is a transition state rather than a local minimum.

This transition state does not appear to be an intermediate in the conversion of I to either III or IV. From II-S, a disrotatory twist of the methylene groups in either a positive or negative direction will give rise to I.

For the I to III pathway it was hoped that a concerted motion in which a B–C bond of I is broken and an ajacent carbon hydrogen migrates toward the boron would result in structure III. However, all reasonable distortions of I to produce such a motion resulted in structures which optimized back to I.

This suggests that the barrier to the above motion may be substantial. An estimate of this barrier was obtained by opening the B–C–C angle of I by 10°, holding it fixed and optimizing the geometry with respect to the remaining parameters. The resulting energy was 56.4 kJ/mol, (3-21 G) above the energy of I. After correlation (MP4/6-31G**) this barrier was reduced to 36.2 kJ/mol indicating a barrier of at least that amount.

While the pathway from structure I to structure IV was not fully determined, much was learned of a possible mechanism by which the cyclic structure I might open to give the lower energy structure IV. The conversion appears to take place via a concerted motion in which the C–C bond breaks as the boron hydrogen migrates toward the carbon opposite the incipient B–C double bond. As the ring opens the angle Θ increases and the energy of the molecule increases. At $\Theta = 82.31$ the energy is 71.9 kJ/mol (3-21G) above the energy of I. After correlation this difference becomes 54.1 kJ/mol (MP4/6-31G**) and serves as a lower bound to the activation energy for the inter-conversion.

From $\Theta \simeq 95$ to $\Theta \simeq 130$ the SCF procedure fails to converge indicating a state crossing in this region. This is not unexpected considering the different types of bonding in the cyclic structure as compared with structure IV.

Boriranes as synthetic intermediates

Rearrangement activation energies of a magnitude of 80 kJ/mol are required if boriranes are to be observed and serve as useful synthetic intermediates at temperatures routinely accessible to most chemists. The strength of B–O and B–F bonds probably precludes the migration of F or OR (R = H, alkyl or aryl) from boron to carbon by a pathway analogous to I → IV. Calculations on *B*-hydroxy borirane and *B*-hydroxy vinyl borane show that replacement of H with OH reduces the energy difference between borirane and vinyl borane to 27.2 kJ/mol. To the extent that transition state energy changes parallel those of product energy changes, substitution of boron by OR should increase the activation energy for borirane to vinyl borane rearrangement.

Conclusion

The results of this investigation indicate that structure I, borirane is a true minimum on the C_2H_5B energy surface. Any distortion of I towards one of its probable interconversion products increases the energy of I by at least 33 kJ/mol. This is in contrast to the isoelectronic cyclopropyl cation ($C_3H_5^+$) which opens spontaneously through the disrotatory motion of its methylene hydrogen atoms.

A localization study of the bonding in borirane indicates that the C–C σ-bonding orbital is lower in energy than the B–C σ-bonding orbitals. The breaking of this bond during the ring opening process results in the destabilization of the planar, open-ring form relative to borirane. Apparently, any stabilization from the formation of the π system does not compensate for the loss of the C–C bond.

Boriranes do represent reasonable synthetic objectives. Substitution at boron by OR, or other strong π electron donating groups, may help to increase the kinetic stability of the borirane and, of course, render structures such as IV unlikely.

Acknowledgements

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