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Orbital Tilting Due to Destabilizing Four-electron and Stabilizing Two-electron Orbital Interactions. An Elucidation of *Exo-endo*-nonequivalency of π-MO Extension of Norbornene

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A new concept, "Orbital Tilting," leading to hybridization change, was introduced on the basis of the destabilizing and the stabilizing secondary orbital interaction. The predominant π-MO extension of norbornene in the *exo*-direction was elucidated by application of the concept to the orbital system.

The *exo*-stereoselectivity in electrophilic addition to norbornene has been ascribed to π-HOMO extending predominantly in the *exo*-direction.[1] The nonequivalent orbital extension was rationalized in terms of the perturbation of etheno-π and -σ orbital through the orbital interaction with the methano-bridge.[1a,b] The orbital interaction results in the mixing between the unperturbed etheno-π and the etheno-σ MO or the basis 2p and 2s AO, which is the ground of the nonequivalency of the π-MO extension. Thus the *exo-endo* nonequivalency of the π-MO extension can be understood as a problem of hybridization change.

According to Woodward and Hoffmann,[2] the cyclization of conjugated polyenes such as that of *s-cis*-butadiene to cyclobutene is represented in terms of the inclinations of both terminal methylenes. The inclination of methylene groups implies a tilt of orbitals, and the HOMO-LUMO interaction scheme[3] and other MO-theoretical treatments[2,4] rationalize the conrotatory cyclization of butadiene. In these treatments, however, only the tilt of p-π-type orbitals are considered; thus, the concomitant hybridization change is not handled in principle.[5]

In the present paper, on the basis of the HOMO-LUMO maximum overlapping principle,[3] we introduce a new concept, "Orbital Tilting," which involves the tilt of (s,p)-hybrid σ-type orbitals and leads to hybridization change.[6] The norbornene π-MO with predominant extension in the *exo*-direction is derived by application of the concept to an orbital system with an originally equivalent π-MO extension.

Results

Orbital Tilting and Hybridization Change. Let us consider a chemical system involving a methylene carbon (in sp^2 hybridization) bonded to another carbon in sp^2-sp^2 σ mode (χ_1 for the sp^2-hybrid AO of the methylene carbon, χ_2 for that of the other) and a group with an sp^2-hybrid orbital (χ_3) which is going to overlap in a σ symmetry with the p-type orbital (p) located in the methylene carbon (Fig. 1). Since a localized bonding σ_{CC} level is underlain by a bonding σ_{CH} level and the antibonding counterpart of σ_{CC} underlies that of σ_{CH} in ordinary hydrocarbons,[7] the order of orbital levels of the system under consideration is given as $\sigma^*_{CH} > \sigma^*_{CC} (=\chi_1-\chi_2) > p > \chi_3 > \sigma_{CC} (=\chi_1+\chi_2) > \sigma_{CH}$. In this orbital system, χ_3 can interact with p upon approach and also with the localized σ-type orbitals. When the interaction between χ_3 and the σ orbitals located in the C–H bond regions is neglected as a first approximation,[8] the σ^*_{CC} orbital takes part as the next LUMO (NLUMO) or LUMO in the orbital interaction leading to hybridization change. According to the occupancy of p and χ_3,[9] four types of orbital interaction can be applied to the orbital system represented in Fig. 1: (1) A two-electron system (both χ_3 and p are unoccupied); (2) a four-electron system (χ_3 is occupied and p unoccupied); (3) a four-electron system (χ_3 is unoccupied and p occupied); (4) a six-electron system (both χ_3 and p are occupied).[10]

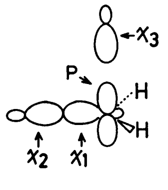
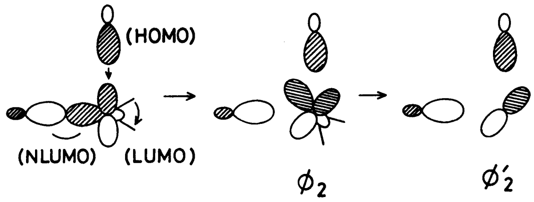


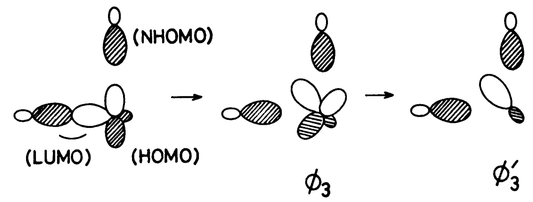
Fig. 1. Four-center orbital system leading to orbital tilting.

On the basis of the frontier orbital[3] or the perturbation concept,[11] these orbital systems can be treated in the following way. In Case 2, the interaction of χ_3 (HOMO) with p (LUMO) stabilizes the system, which is represented by the in-phase combination of χ_3 and p. Secondary stabilization may arise from the overlap between χ_3 (HOMO) and σ^*_{CC} (NLUMO). The orbital arrangement of σ^*_{CC} should be selected in such a way that χ_3 and χ_1 are in-phase (χ_3 and χ_2 are out-of-phase) (Fig. 2a); because χ_1 is located closer to χ_3 than χ_2 is and the in-phase overlap between χ_1 and χ_3 stabilizes the system. In this situation, as shown in Fig. 2a, the interaction of χ_1 with χ_3 and that of χ_2 with the bottom lobe of p are attractive. The HOMO-LUMO-NLUMO maximum overlap may be realized[12] by orbital tilting when the methylene group is inclined in the symmetrically bisecting plane to the configuration in which the two hydrogen atoms are more remote from the approaching group with local χ_3. Since χ_1 becomes orthogonal to the out-of-phase combination of χ_2 and χ_3 in the MO representation after orbital tilting (ϕ_2 in Fig. 2a), ϕ_2 should be revised to ϕ_2', which is just the delocalized HOMO in the orbital system. In Case 3, the orbital system is occupied in the reverse manner of that in Case 2; however, since p (HOMO) interacts with σ^*_{CC} (NLUMO) through χ_3 (LUMO), the mode of orbital interaction should be equivalent to that of Case 2.

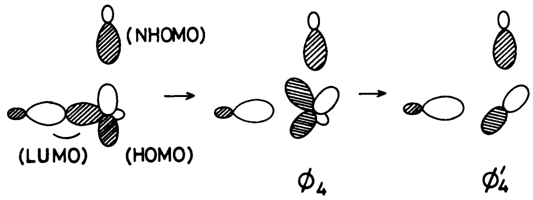
In Case 4, the interaction of χ_3 (NHOMO) with p



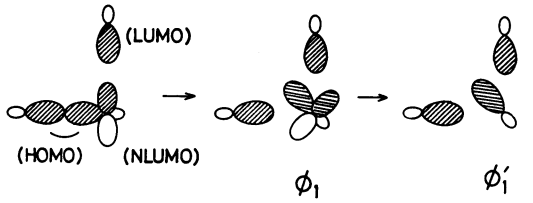
(a) Interaction of σ_{CC}^* as NLUMO.



(b) Interaction of σ_{CC}^* as LUMO (Type I).



(c) Interaction of σ_{CC}^* as LUMO (Type II).



(d) Interaction of σ_{CC} as HOMO.

Fig. 2. Orbital tilting in the four-center orbital system.

(HOMO) destabilizes the system; this situation is represented by the out-of-phase combination of χ_3 and p. This representation is consistent with that of the semi-delocalized HOMO in the initial state. For stabilization, the following two alternative terms are available: One may arise from the overlap between p (HOMO) and σ^*_{CC} (LUMO), in which χ_2 and the bottom lobe of p are in-phase (Type I), and the other may arise from the overlap between χ_3 (NHOMO) and σ^*_{CC} (LUMO), in which χ_3 and χ_1 are in-phase (Type II). Since the magnitude of stabilization is dependent upon both the extent of orbital overlapping and the difference between the energy levels of orbitals, these circumstances are somewhat equivocal. However, the former stabilization term is probably dominant in view of the closer energy level of p to σ^*_{CC} and of the bonding character between χ_3 and χ_2. The situation of orbital interaction in this manner is given in Fig. 2b. The interaction of p with χ_2 becomes attractive; the HOMO-LUMO maximum and the HOMO-NHOMO minimum overlap may be achieved compatibly by orbital tilting in a manner similar to that of Cases 2 and 3. In the MO representation after orbital tilting (ϕ_3 in Fig. 2b), p is orthogonal to the in-phase combination of χ_2 and χ_3; accordingly, ϕ_3 should be revised to ϕ'_3, which is the delocalized HOMO in this orbital system. For this orbital system, the delocalized LUMO (ϕ'_4) can be derived in the same way from the alternative orbital representation in which σ^*_{CC} is given in such a way that χ_3 and χ_1 are in-phase (Fig. 2c).

For Case 1, σ_{CC} is the HOMO and χ_3 and p are the LUMO and the NLUMO, respectively. In the MO representation, χ_3 and σ_{CC} are in-phase; similarly, χ_3 and p are in-phase, for the in-phase combination of χ_3 and p designates the semi-delocalized LUMO. The orbital interaction can be treated analogously; this treatment is given in Fig. 2d. Since ϕ'_1 is the HOMO for the four-center two-electron system, it lies in the bottom level. Similarly, from the fact of electron occupation, it is evident that the energy ordering is $\phi'_1<\phi'_2<\phi'_3<\phi'_4$.[13]

On the one hand, since the constituent p and χ_1 in ϕ_1—ϕ_4 are based on the atomic p and the hybrid sp^2 orbital, they can be re-hybridized into a new equivalent basis set, $(\lambda\chi_1-p)/\sqrt{1+\lambda^2}$ $(=\chi_4)$ and $(\chi_1+\lambda p)/\sqrt{1+\lambda^2}$ $(=\chi_5)$. In the orbital system after re-hybridization, χ_4 overlaps with χ_2 and χ_5 with χ_3, where $\lambda\approx1$. The orbital system after re-hybrodization is represented schematically in Fig. 3 by an example.[14] Consequently, the two hybridization-changed C–C σ bonds are represented with the sets of bond orbitals, $(\chi_2+\chi_4)/\sqrt{2}$ and $(\chi_2-\chi_4)/\sqrt{2}$, and $(\chi_3+\chi_5)/\sqrt{2}$ and $(\chi_3-\chi_5)/\sqrt{2}$, respectively.

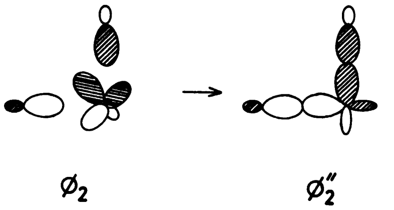


Fig. 3. Re-hybridization.

Predominant Extension of π-HOMO and π-LUMO in the Exo-direction in Norbornene System. We assume first a bicyclo[2.2.1]hept-2-ene structure in which its π-MO originally extends *exo-endo*-equivalently. For this system, the hyperconjugative four-electron interaction between the methano-bridge methylene and the double bond (through space) may be considered. As has been well known, the hyperconjugative effect of simple alkyl and alkylene groups is electron-donating.[15] The hypothetical unperturbed bicycloheptene system is represented in Fig. 4 with three localized π_{CH_2} orbitals (χ_{11}, χ_{12}, and χ_{13}) and one π orbital. In this orbital system, the three localized π_{CH_2} orbitals give a new set of semi-delocalized

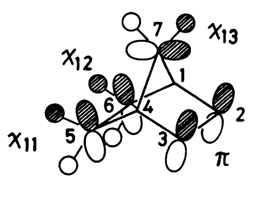
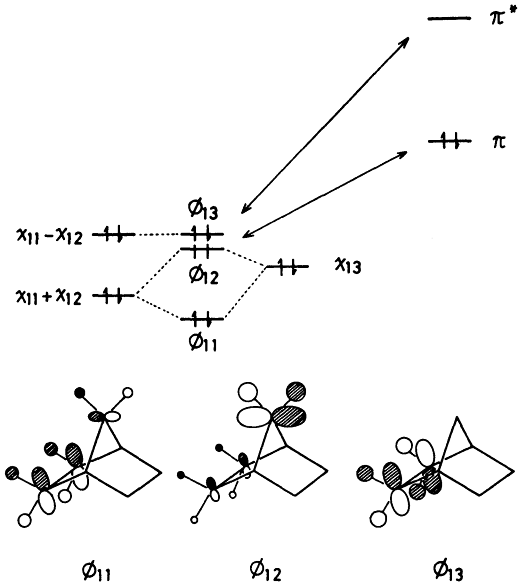


Fig. 4. Bicyclo[2.2.1]hept-2-ene system represented with unperturbed π and π_{CH_2} orbitals.



Scheme 1.

orbitals, ϕ_{11}, ϕ_{12}, and ϕ_{13}, according to the orbital interaction principle[11] (Scheme 1).

Since the orbital interaction between χ_{11} and χ_{12} is stronger than those of other combinations, ϕ_{13} should be underlain by ϕ_{12}, in which χ_{13} is the predominant contributor. According to the property of orbital symmetry, ϕ_{12} can interact with π in a four-electron fashion and ϕ_{13} with π^* in a two-electron fashion, and the interaction between ϕ_{11} and π can be considered weak and negligible in view of the difference in energy level.[16] The fact that the energy levels of ϕ_{12} and π are closer than the energy levels of ϕ_{13} and π^* suggests that the interaction of ϕ_{12} with π is dominant over that of ϕ_{13} with π^*. In this orbital system, the decrease of NHOMO (ϕ_{12})-HOMO (π) overlap and the increase of HOMO (ϕ_{13})-LUMO (π^*) overlap, both leading to the stabilization of the system, may be realized by orbital tilting, when the etheno group is inclined around the C_2–C_3 σ axis in the direction from the *exo-* to the *endo-*side to a certain extent keeping the C_2–C_3 and the two C–H σ bonds unchanged. The localized σ_{CC} bond orbitals located in C_1–C_2 and C_3–C_4 ought to be deformed by orbital tilting because, without this deformation, the etheno group cannot be inclined at all while the C_2–C_3 and the two C–H bonds are conserved.

When the σ orbitals located in C_1–C_2 and C_3–C_4 are represented in a semi-delocalized manner on the basis of sp^2 hybrids, the resulting low-lying vacant level (σ_{13}^*) may interact, upon orbital tilting, with ϕ_{12} in a stabilizing manner and with the low-lying filled level (σ_{11})[17] in a destabilizing manner. The stabilization arising from the interaction of ϕ_{12} with σ_{13}^* can be considered to dominate over the destabilization arising from that with σ_{11} in view of energy-level closing; however, both terms may be small because of their weak interaction. The MO representation for the orbital interaction between ϕ_{12} and π is given in Fig. 5, in which the low-lying vacant level (σ_{13}^*) is represented. The situation of orbital interaction resembles that of Case 4 described above, except that no formation of bond is involved; thus, the orbital system after tilting can be treated in the same manner and each constituent sp^2 hybrid and p orbital involved in σ_{13}^* and π are rehybridized to give a new set of unequally hybridized orbitals. One pair of the new hybrids, consisting of a large fraction of the original sp^2 hybrids and a small fraction of the p orbital, lie in the $C_1C_2C_3C_4$ coplane and overlap with the local hybrid orbitals in C_1 and C_4 to lead to the generation of $\sigma_{13}^{*\prime}$ which corresponds to σ_{13}^*. The low-lying filled level, σ_{11}', is obtained analogously by considering the participation of σ_{11}. The other pair, consisting of a large fraction of p and a small fraction of sp^2 hybrids, should be in-phase and has its predominant extension in the exo-direction unquestionably, as seen in Fig. 5. This in-phase combination of the pair thus obtained (π' in Fig. 5) is the HOMO of norbornene system.

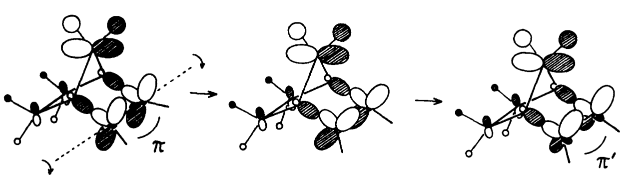
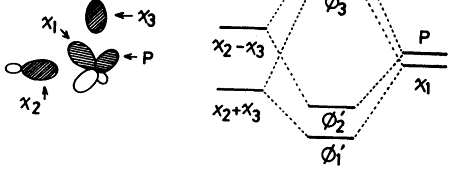


Fig. 5. Derivation of norbornene π-HOMO with predominant extension in the *exo*-direction.

In a similar manner, the LUMO of norbornene with its predominant extension in the exo-direction can be derived from the orbital system involving ϕ_{13}, π^*, σ_{12}, and σ_{14}^*.[18]

Discussion

Orbital tilting does not mean the physical inclination of orbitals (only the shift of nuclei takes place actually), of course, but it merely an artificial device in analogy with orbital hybridization. However, orbital tilting is specified in such a way that the HOMO-HOMO minimum and the HOMO-LUMO maximum overlap may be realized; therefore, this method has its theoretical grounds in the perturbation or the frontier orbital theory. In this connection, it should be noted that the delocalized MO's, ϕ_1', ϕ_2', ϕ_3', and ϕ_4', obtained above by orbital tilting can be given alternatively by the qualitative LCAO method and that the relative energy levels are consistent with the assignment stated above (Scheme 2). As seen in Fig. 3, the re-hybrids by orbital tilting



$\phi_2' = \chi_2 - \chi_3 + P$ $\phi_4' = \chi_2 - \chi_3 - P$

$\phi_1' = \chi_2 + \chi_3 + \chi_1$ $\phi_3' = \chi_2 + \chi_3 - \chi_1$

Scheme 2.

are in sp^5 hybridization, which are slightly different from the situation actually observed. This difference results from neglecting the interaction of σ orbitals located in the C–H bond regions, and is not serious.

In the method based on the orbital mixing rule, delocalized orbitals are considered for the purpose of predicting orbital extension[1a,b] or hybridization change,[6] which leads to configuration altering.[19] On the other hand, in the present method, the orbitals are represented in a localized manner and the configuration is altered so that the orthogonality of orbitals may be conserved approximately: The alteration of configuration results in hybridization change. A recognition of hybridization change on the basis of localized MO's may be feasible and reasonable;[20] for the localized MO's represented with bond orbitals correspond best with classical chemical structures and hybridization itself is based on local AO's. The merit of the concept of orbital tilting is the ease with which one can infer the alteration of configuration accompanied by hybridization change or molecular deformation.

As has been seen above, the norbornene π MO with predominant extension in the *exo*-direction can be derived from the unperturbed etheno-π MO involved in bicyclo[2.2.1]hept-2-ene structure by application of the concept of orbital tilting, due to the secondary interaction with the methano-bridge methylene as the main hyperconjugative entity.[21] Since it is generally accepted that the stability of norbornen-7-ylium ion and the instability of norbornen-7-ide ion are due to the homoconjugation[22] of the ion center with the double bond, the (homo)hyperconjugation of methano-bridge methylene with the double bond can be expected *a priori* in the bicycloheptene structure. On the other hand, if other conditions such as the extent of orbital overlapping can be regarded as equivalent, the hyperconjugative effect of the methano- and ethano-bridge in the neutral system may be dominant over that of methylenes because the energy level of a localized σ_{CC} orbital is higher than that of a localized σ_{CH}. However, from the view point of orbital symmetry, the hyperconjugative effect of methano- and ethano-bridging bond can be expected to operate in the same manner[23] as that of methylene C–H bonds.

The inclination of etheno group around the C_2–C_3 σ axis causes the hydrogen atoms attached to C_2 and C_3 to shift slightly downward from the $C_1C_2C_3C_4$ coplane (Fig. 5): This situation accords with the result of MO-theoretical calculation for norbornene[1c] and for bicyclo[2.2.1]hept-2-yl.[24]

The conformational properties and geometries of small and simple hydrocarbon molecules have been analyzed in terms of the four-electron destabilizing or the two-electron stabilizing interaction *via* hyperconjugation;[25] the same principle should be applicable also to more complex, rigid molecules. Thus, the hyperconjugative effect on the double bond results in the molecular deformation, which is the origin of the predominant extension in the *exo*-direction for π MO in norbornene system.

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2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York (1969).

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4) H. Zimmerman, *Acc. Chem. Res.*, **4**, 272 (1971); M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **12**, 36 (1971); W. A. Goddard III, *J. Am. Chem. Soc.*, **94**, 793 (1972).

5) In the reverse reaction (the ring opening), the rotation of sp^3 hydrids are considered, but their hybridization change has not also been dealt with.

6) The hybridization change in the nucleo- or electrophilic addition to an unsaturated carbon has been dealt with by Fukui (*Kagaku To Kogyo*, **29**, 470 (1976); "Kagaku-hanno To Denshi No Kido," Maruzen, Tokyo (1976), p. 188) on the basis of the sigma-pi interaction (K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **39**, 2116 (1966).

7) W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals," Academic Press, New York (1973), p. 14.

8) Neglecting the interaction of σ orbitals located in the C–H bonds implies that the two σ_{CH} and the two σ^*_{CH} levels are regarded as orthogonal to other levels throughout the course of reaction.

9) Single occupation is excluded from the scope of this argument.

10) In all cases, the number of electrons includes two electrons which occupy the σ_{CC} orbital.

11) Ref. 7, p. 10.

12) The destabilization arising from the decreased in-phase overlap between χ_3 and p is repaired by the stabilization arising from the increased in-phase overlap between χ_2 and p.

13) The energy ordering is in accord with that of group orbitals for CH_2: $\sigma_{CH_2} < \pi_{CH_2} < \sigma^*_{CH_2} < \pi^*_{CH_2}$. See Ref. 7, p. 7.

14) MO's ϕ_1''—ϕ_4'', which are equivalent to ϕ_1—ϕ_4, are formulated approximately as follows:

$$\begin{aligned}\phi_1'' &= (\chi_3+\chi_5)/2 + (\chi_2+\chi_4)/2,\\ \phi_2'' &= (\chi_3+\chi_5)/2 - (\chi_2+\chi_4)/2,\\ \phi_3'' &= (\chi_3-\chi_5)/2 + (\chi_2-\chi_4)/2,\\ \phi_4'' &= (\chi_3-\chi_5)/2 - (\chi_2-\chi_4)/2.\end{aligned}$$

15) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," John Wiley and Sons, New York (1976), p. 48.

16) From the fact that ϕ_{12} has its largest amplitude in C_7, the hyperconjugative effect of methano-bridge methylene should predominate over that of ethano-bridge methylenes.

17) The high-lying counterparts, σ_{12} (filled) and σ_{14}^* (vacant), interact with π^* upon orbital tilting.

18) The σ type orbitals, σ_{12}' and $\sigma_{14}'^*$ corresponding to σ_{12} and σ_{14}^*, are also obtained.

19) That is to say, the alteration of configuration is treated as the result of a hybridization change.

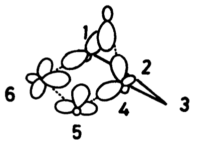
20) Another advantage of identifying a chemical process on the basis of localized MO's has been in a method for predicting pericyclic reactions: S. Ito, A. Kakehi, and Y. Tanaka, *Bull. Chem. Soc. Jpn.*, **48**, 2855 (1975).

21) The predominant extension of bicyclo [2.1.0]pent-2-ene in the *exo*-direction[1a,b] can be likewise derived on the basis of the secondary four-electron interaction between π and the

Walsh σ_{CC} orbital extending in the *exo*-direction.

22) S. Winstein, *Quart. Revs.*, **23**, 141 (1969). See also: J. B. Grutzner and W. L. Jorgensen, *J. Am. Chem. Soc.*, **103**, 1372 (1981); E. Kaufmann, H. Mayr, J. Chandrasekhar, and P. v.R. Schleyer, *ibid.*, **103**, 1375 (1981); and references cited therein.

23) The same result can be obtained by orbital tilting, when the σ MO's for the methano- and the ethano-bridging bonds are represented with group-type orbitals (shown below) in a semi-delocalized manner, or with each (2s, 2p) hybrid located in C_5, C_6, and C_7 by postulating that the interaction between π MO and the local sp^2-type hybrids in C_1 and C_4 are very weak.



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