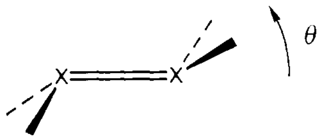
Trans Bending at Double Bonds. Occurrence and Extent

Jean-Paul Malrieu and Georges Trinquier*

Contribution from the Laboratoire de Physique Quantique, C.N.R.S., U.A. 505, Université Paul-Sabatier, 31062 Toulouse Cedex, France. *Received December 7, 1988*

Abstract: A simple rule for the occurrence of trans-bent distortions at homopolar double bonds is derived from an elementary molecular orbital model treating σ–π mixing. In $R_2X{=}XR_2$, the distortion occurs when the singlet–triplet separation (ΔE_{ST}) of the constituent carbenoid XR_2 is larger than a quarter of the X=X $\sigma + \pi$ bond energy ($E_{\sigma+\pi}$). The same condition has been previously proposed from a valence bond treatment (ref 1). The present model further defines the domain of existence of a direct X=X link by $-{}^1/_2E_{\sigma+\pi} < \Delta E_{ST} < {}^1/_2E_{\sigma+\pi}$. The trans-bent geometry occurs therefore when ${}^1/_4E_{\sigma+\pi} \leqslant \Delta E_{ST} < {}^1/_2E_{\sigma+\pi}$. Within this interval, the trans-bending angle θ is estimated as $\theta = \arccos(2-4\Delta E_{ST}/E_{\sigma+\pi})$, which underlines the high sensitivity of the geometry to ΔE_{ST} near the lower bound of the interval. Simple functions are also proposed for force constants and barrier to planarity.

Some double bonds do not exhibit the classical planar geometry of olefins but rather have trans-bent structures, **1**, with pyramidalization of the XR_2 groups. The most famous and simplest



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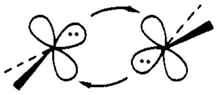
examples concern the homopolar analogues of ethylene involving heavier elements of group 14, i.e., Si_2H_4, Ge_2H_4, and Sn_2H_4 (for reviews, see ref 1–3). For disilene, most sophisticated calculations predict a bending angle of about 36°, with an energy stabilization of $\approx$2 kcal/mol.[4–6] The results are quite similar and more pronounced for digermene.[7,8] For distannene, the distortion is stronger ($\theta \approx 50°$) as found from experimental structures of derivatives and from theoretical calculations.[6,8] Similar distortions may also occur in C=C double bonds of cumulenones and ketenes.[1] A simple rationale for such distortions has been proposed, and the following rule of occurrence has been suggested.[1]

Rule: Trans-bent distortion of a double bond $R_2X{=}YR'_2$ occurs when the carbenoid fragments R_2X: and $:YR'_2$ have a singlet ground state and when the sum of the singlet–triplet separations in these divalent species is larger than half of the total bond energy of the X=Y double bond:

$$\Sigma\Delta E_{ST} \geqslant {}^1\!/_2E_{\sigma+\pi} \qquad (1)$$

This simple rule has been shown to work for all homopolar double bonds as long as the XR bonds do not undergo π-conjugation effects. Further sophistication has been proposed to treat the cases where the carbenoid substituents bear lone pairs, but the present work will concentrate on the simplest case.

Condition (1) was obtained from a model which assumed that the distorted double bond is built from interacting singlet carbenes. The n_σ pair of one species partly delocalizes into the empty p_π atomic orbital of its partner, assuming a geometry with unique 45° bending angle, **2**. This structure is assumed to represent a local energy minimum. Its energy is estimated from valence bond (VB) considerations and is compared to that of a classical planar $\sigma + \pi$ double bond occurring between two triplet carbenes, **3**. Our VB approach assumed the existence of a questionable avoided crossing between these two VB structures. Their interaction, which should remain weak, was neglected. The model further introduced rather crude hypotheses about the interactions of the XR_2 fragments and was unable to explain why the bending angle increases when the difference between the two members of relation (1) increases.



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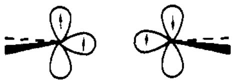

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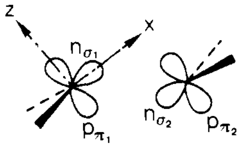
The present paper tries to give an alternative derivation of condition (1) from simple molecular orbital (MO) arguments. One-electron calculations such as EHT calculations are able to predict the trans-bent structures of digermene or distamene, and this has been quantitatively interpreted in terms of σ–π mixing.[9,10] Analytical derivation of relation (1) within an MO scheme would therefore be welcome. The demonstration will be limited here to homopolar systems $H_2X{=}XH_2$. The derivation will require drastic simplifications. Although it provides qualitative pictures which are necessary for chemical interpretation, it should not be taken too literally, and the analytical expressions obtained do not claim to be able to substitute accurate ab initio treatments.

Basic Derivation

In a molecular orbital scheme, bending introduces two opposing effects: (1) a weakening of the σ and π MOs and (2) a stabilizing mixing of orbitals: σ with π^* and π with σ^*. In order to study this in more detail, the atomic orbitals (AO) are defined in the coordinate system of the rotating XH_2 fragments, **4**. When these



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orbitals are properly orthogonalized, one may keep, at zero order,

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[1] Trinquier, G.; Malrieu, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 5303.
[2] Trinquier, G.; Malrieu, J. P. In *The Chemistry of Double-Bonded Functional Groups*; Patai, S., Ed.; John Wiley and Sons: New York, 1989; Supplement A, Vol. 2.
[3] (a) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1. (b) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201.
[4] Somasundran, K.; Amos, R. D.; Handy, N. C. *Theor. Chim. Acta* **1986**, *70*, 393.
[5] Teramae, H. *J. Am. Chem. Soc.* **1987**, *109*, 4140.
[6] Trinquier, G.; Malrieu, J. P. Submitted for publication in *J. Am. Chem. Soc.*
[7] Trinquier, G.; Malrieu, J. P.; Rivière, P. *J. Am. Chem. Soc.* **1982**, *104*, 4529.
[8] Golberg, D. E.; Hitchcok, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387.
[9] Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 166.
[10] See also Appendix I of ref 1 and ref 8.

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the same definition for σ and π as in the planar geometry:

$$\sigma = {}^1/_{\sqrt{2}}(n_{\sigma1} + n_{\sigma2})$$

$$\sigma^* = {}^1/_{\sqrt{2}}(n_{\sigma1} - n_{\sigma2})$$

$$\pi = {}^1/_{\sqrt{2}}(p_{\pi1} + p_{\pi2})$$

$$\pi^* = {}^1/_{\sqrt{2}}(p_{\pi1} - p_{\pi2})$$

The energy weakening of the σ and π MOs when bending takes place is due to the reduction of the off-diagonal elements of the monoelectronic operator $F_\sigma = \langle n_{\sigma1}|F|n_{\sigma2}\rangle$ and $F_\pi = \langle p_{\pi1}|F|p_{\pi2}\rangle$.

This effect alone is, of course, destabilizing. However, the second effect is stabilizing through σ–π mixing. With respect to the inversion center of the molecule, the π and σ^* orbitals are both antisymmetrical, **5** (both have b_u character), while the σ and π^* orbitals are both symmetrical, **6** (both have a_g character). So, as soon as the molecule enters a trans-bent deformation, π will mix with σ^* and σ will mix with π^*. This stabilizing effect *may or may not* compensate the intrinsic weakening of the σ and π bonds. It will only do so if the interaction is large enough. Let us try therefore to quantitize these two effects.

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Level Spacing and Domain of Double Bonding. The spacing of the orbitals for planar and nonplanar ($\theta \neq 0$) geometries is schematized in Figure 1. Let us call ϵ_n and ϵ_p the energies of the n_σ and p_π orbitals of the R_2X: divalent species. If F_σ and F_π are the off-diagonal elements of the monoelectronic operator, the orbital energies associated to our four molecular orbitals can be approximated as

$$\epsilon_\sigma = \epsilon_n + F_\sigma$$

$$\epsilon_{\sigma^*} = \epsilon_n - F_\sigma$$

$$\epsilon_\pi = \epsilon_p + F_\pi$$

$$\epsilon_{\pi^*} = \epsilon_p - F_\pi$$

(remember that ϵ and F are negative quantities). The energy differences

$$\Delta_{\pi\sigma^*} = \epsilon_{\sigma^*} - \epsilon_\pi$$

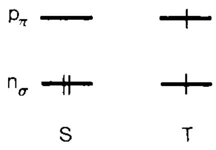
$$\Delta_{\sigma\pi^*} = \epsilon_{\pi^*} - \epsilon_\sigma$$

are therefore written as

$$\Delta_{\pi\sigma^*} = (\epsilon_n - \epsilon_p) - (F_\sigma + F_\pi) \tag{2}$$

$$\Delta_{\sigma\pi^*} = -(\epsilon_n - \epsilon_p) - (F_\sigma + F_\pi) \tag{3}$$

In a one-electron scheme $(\epsilon_n - \epsilon_p)$ may be related to the singlet–triplet separation ΔE_{ST} in the carbenoid **7**:



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$$\Delta E_{ST} = \epsilon_p - \epsilon_n = -(\epsilon_n - \epsilon_p)$$

We shall use, in the following, ΔE_{ST} rather than $(\epsilon_n - \epsilon_p)$ since in the previous work, based on a VB-type approach, this quantity naturally emerged from the derivation.[1] On the other hand, the singlet–triplet splitting ΔE_{ST} is a fundamental observable of the XR_2 carbene-type fragments which are the building blocks of the double bond. Moreover, this quantity, ΔE_{ST}, integrates some subtle bielectronic effects which are neglected in the present MO scheme.

ΔE_{ST} will be positive and large if the σ lone pair has a much deeper energy than the p_π AO. The energy level separations (2) and (3) are now written as

$$\Delta_{\pi\sigma^*} = -\Delta E_{ST} - (F_\sigma + F_\pi) \tag{4}$$

$$\Delta_{\sigma\pi^*} = \Delta E_{ST} - (F_\sigma + F_\pi) \tag{5}$$

Since the energies of the σ and π bonds can be expressed as

$$E_\sigma = -2F_\sigma$$

$$E_\pi = -2F_\pi$$

$$E_{\sigma+\pi} = E_\sigma + E_\pi = -2(F_\sigma + F_\pi) \tag{6}$$

(by definition the bond energy is a positive number), the differences (4) and (5) now become

$$\Delta_{\pi\sigma^*} = {}^1/_2 E_{\sigma+\pi} - \Delta E_{ST} \tag{7}$$

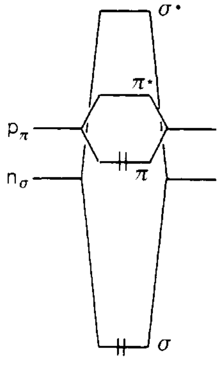
$$\Delta_{\sigma\pi^*} = {}^1/_2 E_{\sigma+\pi} + \Delta E_{ST} \tag{8}$$

As long as we have a $\sigma\pi\pi^*\sigma^*$ ordering, which is necessary to preserve a double-bonding scheme, these differences must be positive. The condition $\Delta_{\sigma\pi^*} > 0$ is always satisfied since π^* is always above σ, in any case. From (8) it implies

$$\Delta E_{ST} > -{}^1/_2 E_{\sigma+\pi}$$

which gives a formal lower limit for our reasoning. Note that the triplet carbenes with large negative singlet–triplet separations (for instance CLi_2, CMe_2, CHCHO, and CHCN)[11] always satisfy this condition since for the C=C bond, $-{}^1/_2 E_{\sigma+\pi} \approx -(85\text{–}90)$ kcal/mol.

The condition $\Delta_{\pi\sigma^*} > 0$ means that σ^* is above π, as in **8**. If we had a $\pi > \sigma^*$ ordering, as in **9**, the $\sigma + \pi$ double-bonding scheme would be destroyed, resulting in no more direct binding between the X atoms in $R_2X{=}XR_2$. From (7), this condition leads to



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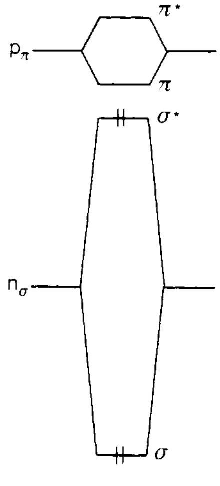

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$$\Delta E_{ST} < {}^1/_2 E_{\sigma+\pi} \tag{9}$$

If the energies for the Si=Si, Ge=Ge, or Sn=Sn bonds are taken

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[11] Davidson, E. R. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; p 73.

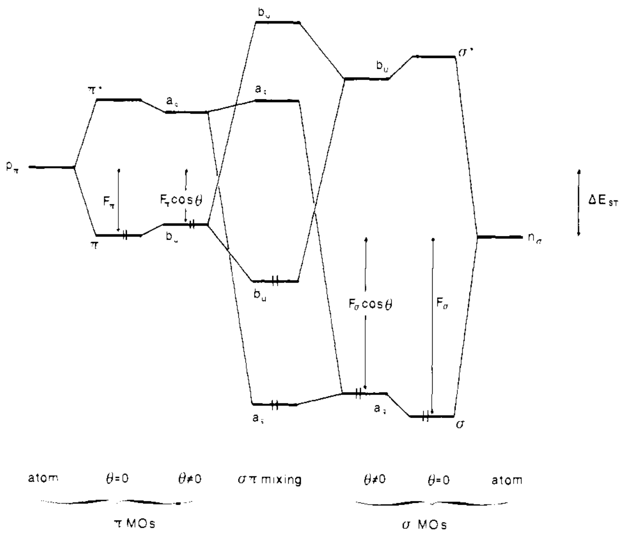
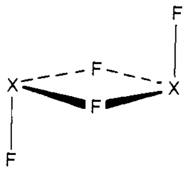


Figure 1. Simplified molecular orbital diagram showing how the σ–π mixing occurs when a planar double bond is trans-bent distorted. On the right-hand side, the σ bond is built from the n_σ orbitals on each carbenoid fragment. On the left-hand side, the π bond is built from the p_π orbitals on each carbenoid fragment. Then, these levels are perturbed by the bending. Lastly, in the middle, the σ and π orbitals are properly mixed according to their symmetry. The n_σ–p_π separation is proportional to ΔE_{ST}.

within 60–80 kcal/mol, the upper limit for the domain of existence of a direct X=X link would then be

$$\Delta E_{ST} < 30\text{–}40 \text{ kcal/mol}$$

Beyond this limit, we would expect no double bond, be it planar or trans bent. Actually this is what happens in Si_2F_4 and Ge_2F_4 which both adopt a doubly bridged structure, **10**, in which the



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fragments are bound through XFX bridges instead of an X=X link.[12,13] SiF_2 and GeF_2 fragments are known to have large singlet–triplet separations: ΔE_{ST} = 73 kcal/mol in SiF_2[14] and 74 kcal/mol in GeF_2.[17] These values happen to be close to the *entire* corresponding X=X bond energies, so condition (9) is largely satisfied. The lead dichloride dimer is another example of a doubly bridged structure,[18,19] which fits with the expected large ΔE_{ST} in $PbCl_2$.

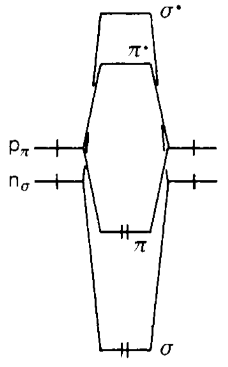
We have therefore defined an interval within which a double bond X=X can exist—its geometry being planar or not:

$$-\tfrac{1}{2}E_{\sigma+\pi} < \Delta E_{ST} < \tfrac{1}{2}E_{\sigma+\pi}$$

Another consequence of the $\sigma\pi\pi^*\sigma^*$ ordering is that π and σ^* are always much closer in energy than σ and π^* (see Figure 1):

$$\Delta_{\pi\sigma^*} < \Delta_{\sigma\pi^*}$$

The main mixing will therefore occur between π and σ^*, and we shall ignore hereafter the other mixing σ–π^*. There is a further reason for not taking σ–π^* mixing into account. Going down column 14, ΔE_{ST} increases, but the π bond strength ($|F_\pi|$) decreases. In an MO diagram, the two effects will cancel and keep $\Delta_{\sigma\pi^*}$ large and unchanged while they make $\Delta_{\pi\sigma^*}$ even smaller, as schematized in **11** and **12**.



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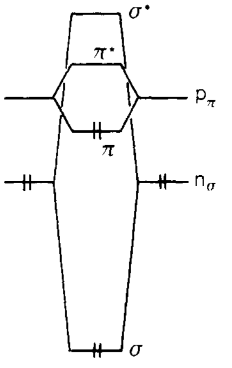

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Let us try to figure out the θ dependence of the zero- and second-order energies, considering σ–π mixing as a perturbation.

σ-π Mixing and Occurrence of Trans Bending. The variation of F with the bending angle θ can be taken as a simple cosine law

$$F_\sigma^{(\theta)} = F_\sigma \cos\theta$$

$$F_\pi^{(\theta)} = F_\pi \cos\theta$$

Therefore the zero-order energy

$$E_0 = \langle \sigma\bar{\sigma}\pi\bar{\pi}|H|\sigma\bar{\sigma}\pi\bar{\pi}\rangle$$

can be written, to a constant, as

$$E_0 = 2(F_\sigma + F_\pi)\cos\theta$$

From (6), this becomes

$$E_0 = -E_{\sigma+\pi}\cos\theta$$

Perturbing the determinant $\Phi_0 = |\sigma\bar{\sigma}\pi\bar{\pi}|$ by an interaction with $\pi \rightarrow \sigma^*$ excited determinants will lead to the second-order energy correction

$$E_2 = -2\frac{\langle\pi|F|\sigma^*\rangle^2}{\Delta_{\pi\sigma^*}^{(\theta)}} = -2\frac{F_{\pi\sigma^*}{}^2}{\Delta_{\pi\sigma^*}^{(\theta)}}$$

For small angles or near planarity, the energy levels are not modified too much:

$$\Delta_{\pi\sigma^*}^{(\theta)} \approx \Delta_{\pi\sigma^*}$$

Therefore E_2 is written as

$$E_2 = -2\frac{F_{\pi\sigma^*}{}^2}{\Delta_{\pi\sigma^*}} \qquad (10)$$

Let us take a simple sine law for the θ dependence of the off-diagonal element $F_{\pi\sigma^*}$ which, on the other hand, can be evaluated from diagonal elements:

$$F_{\pi\sigma^*} = \tfrac{1}{2}(F_\sigma + F_\pi)\sin\theta$$

From (6) this is written as

$$F_{\pi\sigma^*} = -\tfrac{1}{4}E_{\sigma+\pi}\sin\theta \qquad (11)$$

Reporting (7) and (11) in (10) gives

$$E_2 = -\tfrac{1}{4}\frac{E_{\sigma+\pi}{}^2}{E_{\sigma+\pi} - 2\Delta E_{ST}}\sin^2\theta$$

The change in total energy with θ is therefore expressed as

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[12] Si_2F_4 distorts from planar to trans bent (ref 14), but the preferred structure is doubly bridged (ref 15).

[13] Ge_2F_4 is found doubly bridged either from experiment (ref 16) or from calculations (ref 15).

[14] Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 537.

[15] Saint-Roch, B.; Barthelat, J. C. Unpublished theoretical results.

[16] Huber, H.; Kündig, E. P.; Ozin, G. A.; Vandervoet, A. *Can. J. Chem.* **1974**, *52*, 95.

[17] Barthelat, J. C.; Saint-Roch, B.; Trinquier, G.; Satgé, J. *J. Am. Chem. Soc.* **1980**, *102*, 4080.

[18] Schäfer, V. H.; Binnewis, M. *Z. Anorg. Allg. Chem.* **1974**, *410*, 251.

[19] Dewar, M. J. S.; Holloway, M. K.; Grady, G. L.; Stewart, J. P. *Organometallics* **1985**, *4*, 1973.

$$E = E_0 + E_2$$

$$E = -E_{\sigma+\pi}\cos\theta - {}^1\!/\!_4\frac{E_{\sigma+\pi}{}^2}{E_{\sigma+\pi} - 2\Delta E_{\mathrm{ST}}}\sin^2\theta \tag{12}$$

Let us look for the stationary points on the $E = f(\theta)$ potential surface by deriving E with respect to θ

$$\frac{\mathrm{d}E}{\mathrm{d}\theta} = E_{\sigma+\pi}\sin\theta - {}^1\!/\!_2\frac{E_{\sigma+\pi}{}^2}{E_{\sigma+\pi} - 2\Delta E_{\mathrm{ST}}}\sin\theta\cos\theta \tag{13}$$

$$\frac{\mathrm{d}E}{\mathrm{d}\theta} = \left(E_{\sigma+\pi} - {}^1\!/\!_2\frac{E_{\sigma+\pi}{}^2}{E_{\sigma+\pi} - 2\Delta E_{\mathrm{ST}}}\cos\theta\right)\sin\theta$$

and finding the solutions which satisfy

$$\mathrm{d}E/\mathrm{d}\theta = 0$$

A first solution is given by $\sin\theta = 0 \Rightarrow \theta = 0$. For reasons of symmetry, in effect, the planar structure is necessarily a stationary point. If $\theta \neq 0$, a second solution is given by

$$E_{\sigma+\pi} = {}^1\!/\!_2\frac{E_{\sigma+\pi}{}^2}{E_{\sigma+\pi} - 2\Delta E_{\mathrm{ST}}}\cos\theta$$

$$\cos\theta = 2 - \frac{4\Delta E_{\mathrm{ST}}}{E_{\sigma+\pi}} \tag{14}$$

This solution exists if

$$\cos\theta \leq 1 \tag{15}$$

From (14), this yields

$$2\Delta E_{\mathrm{ST}} \geq {}^1\!/\!_2 E_{\sigma+\pi}$$

which is nothing other than condition (1), established from the valence bond treatment.

Discussion

Bending Angle. For a homopolar X=X bond, the trans-bent distortion therefore occurs when

$$\Delta E_{\mathrm{ST}} \geq {}^1\!/\!_4 E_{\sigma+\pi}$$

From all the hypotheses used in our development, we can add to (15) the condition

$$\cos\theta > 0$$

which again leads to (9). The entire domain of existence of a trans-bent double bond given by our model is therefore

$${}^1\!/\!_4 E_{\sigma+\pi} \leq \Delta E_{\mathrm{ST}} < {}^1\!/\!_2 E_{\sigma+\pi}$$

Within this domain, the bending angle θ is given by

$$\theta = \arccos\left(2 - \frac{4\Delta E_{\mathrm{ST}}}{E_{\sigma+\pi}}\right) \tag{16}$$

The bending angle increases with singlet–triplet separation. Its variation is plotted in Figure 2 for a set of bond energies from 20 to 200 kcal/mol. When ΔE_{ST} is close to its lower limit ${}^1/_4 E_{\sigma+\pi}$ the tangent is vertical and θ is extremely sensitive to ΔE_{ST}. This vertical tangent at the origin is also deduced from the derivative of (16):

$$\frac{\mathrm{d}\theta}{\mathrm{d}\Delta E_{\mathrm{ST}}} = \frac{4}{E_{\sigma+\pi}\left\{1 - \left(2 - \dfrac{4\Delta E_{\mathrm{ST}}}{E_{\sigma+\pi}}\right)^2\right\}^{1/2}}$$

At the lower limit of the interval ($\Delta E_{\mathrm{ST}} = {}^1/_4 E_{\sigma+\pi}$, $\theta = 0°$), this derivative tends toward $+\infty$ for whatever value of $E_{\sigma+\pi}$. At the upper limit ($\Delta E_{\mathrm{ST}} = {}^1/_2$, $\theta = 90°$), this derivative tends toward $4/E_{\sigma+\pi}$ and therefore decreases for high $E_{\sigma+\pi}$.

Because of the large sensitivity of θ to ΔE_{ST}, we do not expect to find accurate bending angles from eq 16. Let us test it with the group 14 olefins which satisfy the criterion for trans-bent structure. From literature data for $E_{\sigma+\pi}$ and ΔE_{ST}, we get the values listed in Table I which, as expected, do not accurately fit the angles obtained from correlated or noncorrelated ab initio treatments. To illustrate the problem, we have indicated in Figure 1 the zone corresponding to the bond energies (shaded area) for these heavier analogues of ethylene and to the ΔE_{ST} region for the heavier analogues of methylene.

The extreme sensitivity of θ to ΔE_{ST}, when ΔE_{ST} is close to ${}^1/_4 E_{\sigma+\pi}$, is quite in line with the very flat potential surface for the trans bending in disilene. Ab initio-calculated bending angles range from 0° to 36° according to basis sets and correlation treatments. If $E_{\sigma+\pi} = 72$ kcal/mol, an underestimation of ΔE_{ST} by as little as 1 kcal/mol (as may happen from defects in correlation treatment for instance) would reduce θ from 19° to 0°. On the other hand, when ΔE_{ST} is far from the lower limit of ${}^1/_4 E_{\sigma+\pi}$, small changes in ΔE_{ST} will result in a limited change in θ. Typically, for digermene and distannene, a change of 1 kcal/mol in ΔE_{ST} will alter θ by only 4°. This might clarify why, at the SCF level, discrepancies are so great in calculated bending angles in disilene, whereas the agreement is better, for instance, in distannene (θ = 46°,[8] 49° [6]).

Force Constants. The second derivative of the energy, as obtained from (13), is

$$\frac{\mathrm{d}^2E}{\mathrm{d}\theta^2} = E_{\sigma+\pi}\cos\theta - {}^1\!/\!_2\frac{E_{\sigma+\pi}{}^2}{E_{\sigma+\pi} - 2\Delta E_{\mathrm{ST}}}\cos 2\theta \tag{17}$$

For the planar form ($\theta = 0$) which is always a stationary point, this expression reduces to

$$\frac{\mathrm{d}^2E}{\mathrm{d}\theta^2} = E_{\sigma+\pi}\left(1 - {}^1\!/\!_2\frac{E_{\sigma+\pi}}{E_{\sigma+\pi} - 2\Delta E_{\mathrm{ST}}}\right) \tag{18}$$

As long as $\Delta E_{\mathrm{ST}} < {}^1/_4 E_{\sigma+\pi}$, the force constant is positive and the planar form is a real minimum. For $\Delta E_{\mathrm{ST}} = {}^1/_4 E_{\sigma+\pi}$, the force constant is zero, and when $\Delta E_{\mathrm{ST}} > {}^1/_4 E_{\sigma+\pi}$, it becomes negative, meaning that the planar form is now a maximum (in fact a saddle point) on the potential surface. In the region of planar stability, as expected, the force constant decreases when ΔE_{ST} increases. If we apply this to the ethylene C=C double bond ($E_{\sigma+\pi} = 172$ kcal/mol), we get a trans-wagging force constant of 2.3 mdyn/Å, which is larger than that obtained from a four-electron four-orbital CAS-MCSCF ab initio calculation (1.5 mdyn/Å).[6] For larger values of ΔE_{ST}, relation (18) gives

ΔE_{ST} (kcal/mol)	k (mdyn/Å)
−9	2.3
10	2.1
20	1.9
30	1.5
40	0.3

When the trans-bent structure is the true minimum, the expression of the second derivative is obtained by including (14) in (17), which gives

$$\frac{\mathrm{d}^2E}{\mathrm{d}\theta^2} = 2\left\{E_{\sigma+\pi} - 2\Delta E_{\mathrm{ST}} - \frac{{}^7\!/\!_4 E_{\sigma+\pi}{}^2 + 8\Delta E_{\mathrm{ST}}{}^2 - 8E_{\sigma+\pi}\Delta E_{\mathrm{ST}}}{E_{\sigma+\pi} - 2\Delta E_{\mathrm{ST}}}\right\} \tag{19}$$

When $\Delta E_{\mathrm{ST}} > {}^1/_4 E_{\sigma+\pi}$ the force constant is positive and increases with ΔE_{ST}. It is zero, as expected, when $\Delta E_{\mathrm{ST}} = {}^1/_4 E_{\sigma+\pi}$. In Table I, the force constants evaluated this way are listed and compared with ab initio values. The trends are correctly reproduced. The behavior of the trans-wagging force constants over the entire domain of existence of the double bond scheme is summarized in Figure 3 for a set of $\sigma + \pi$ bond energies. In the planar domain, starting from $\Delta E_{\mathrm{ST}} = -{}^1/_2 E_{\sigma+\pi}$, the trans-wagging force constant decreases down to zero at $\Delta E_{\mathrm{ST}} = {}^1/_4 E_{\sigma+\pi}$. There, the planar form is a saddle point, and the force constant becomes negative and decreases (or increases in absolute value) toward $-\infty$ when ΔE_{ST} tends toward ${}^1/_2 E_{\sigma+\pi}$. At $\Delta E_{\mathrm{ST}} = {}^1/_4 E_{\sigma+\pi}$, the trans-bent form, which is now the true minimum, gives rise to another force constant which is positive. It increases from 0 to $+\infty$ as ΔE_{ST} increases

Table I. Application of Eq 16, 19, and 20 to Heavier Analogues of Ethylene

			bending angle (deg)		wagging force constant[d]		barrier to planarity[a]	
	$E_{\sigma+\pi}$[a,b]	ΔE_{ST}[a,c]	this work	ab initio	this work	ab initio	this work	ab initio
$H_2Si{=}SiH_2$	70–75	18–19	0–24	33–36[e]	0–0.3	1.3[h]	0–0.3	2[i]
$H_2Ge{=}GeH_2$	65	22	50	40–42[f]	1.5		6	4–7[j]
$H_2Sn{=}SnH_2$	60–65	23	54–62	46–53[g]	1.8–2.5	2.7[h]	9–18	8–16[k]

[a] In kcal/mol. [b] See Table I of ref 1 for the origin of bond energies. [c] References 11, 20, and 21 for SiH_2, ref 22 for GeH_2, ref 23 for SnH_2. [d] In mdyn/Å. [e] References 4, 5, and 6. [f] References 8 and 7. [g] References 8, 6, and 24. [h] Reference 6. [i] Reference 4. [j] Estimated from ref 7 and 8. [k] Estimated from ref 6 and 8.

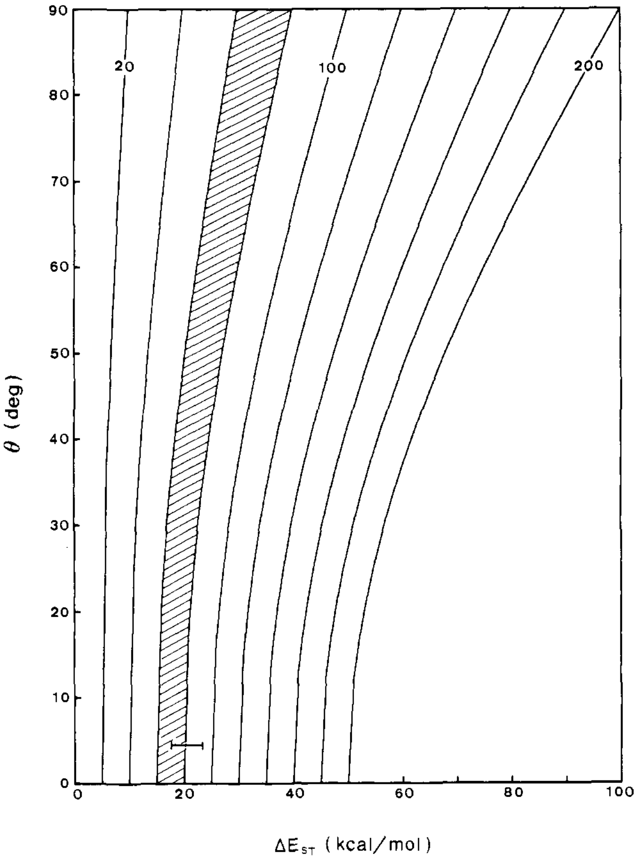

Figure 2. Bending angle versus the singlet–triplet separation as obtained from eq 16 for a set of $\sigma + \pi$ bond energies. These span from 20 kcal/mol (left) to 200 kcal/mol (right) by regular steps of 20 kcal/mol. The shaded area corresponds to $\sigma + \pi$ bond energies of 60–80 kcal/mol, which includes the energies of the Si=Si, Ge=Ge, and Sn=Sn double bonds. The interval ΔE_{ST} = 18–23 kcal/mol includes the singlet–triplet separations in SiH_2, GeH_2 and SnH_2.

from ${}^1/_4E_{\sigma+\pi}$ to ${}^1/_2E_{\sigma+\pi}$. Figure 4 is an enlargement of Figure 3 in a more reasonable domain of validity and application of the model. Note in these two figures that beyond $\Delta E_{ST} = {}^1/_4E_{\sigma+\pi}$, not only are the two curves unsymmetrical (with respect to the x axis) but also their tangent at the splitting point. There, the slopes of the two tangents happen to be constant whatever the value of $E_{\sigma+\pi}$. It is easy to demonstrate from (18) and (19) that they are +8 for the upper curves and −4 for the lower curves.

Barrier to Planarity. The general expression for total energy, eq 12, enables us to analytically express the planarity barrier in trans-bent molecules (or the energy gain due to trans bending). From (12) and (14), this energy difference can be written

$$D = E_{\sigma+\pi} - 4\Delta E_{ST} - \frac{{}^3/_4E_{\sigma+\pi}{}^2 + 4\Delta E_{ST}{}^2 - 4E_{\sigma+\pi}\Delta E_{ST}}{E_{\sigma+\pi} - 2\Delta E_{ST}} \qquad (20)$$

This formula gives quite reasonable evaluations for the barriers as can be seen in Table I. For a set of $E_{\sigma+\pi}$, the curves $D = f(\Delta E_{ST})$ are plotted in Figure 5. Note that the tangents at the origins are all horizontal as can be demonstrated by deriving (20). Now, any change in ΔE_{ST} of SiH_2 will only induce a tiny change in D for disilene.

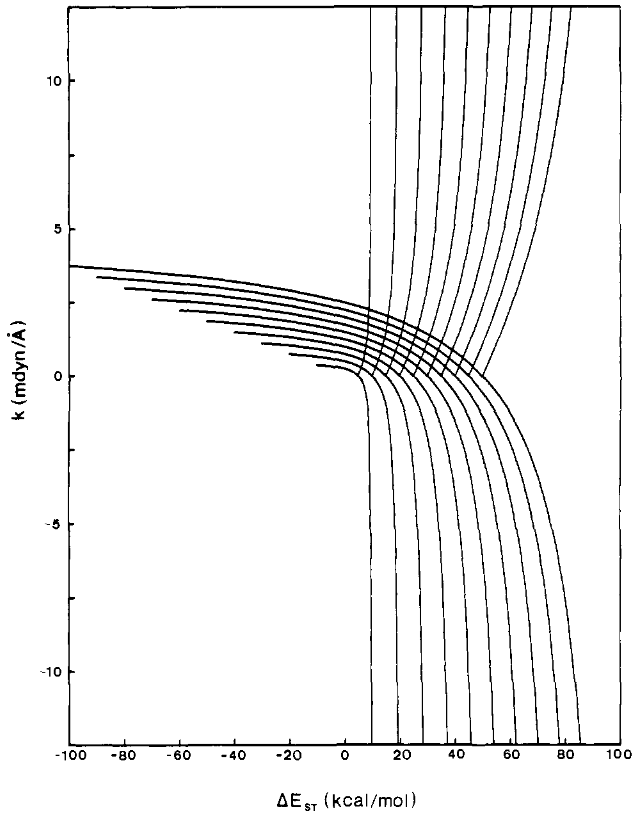

Figure 3. Force constants upon ΔE_{ST} over the entire domain of existence of a double bond scheme. As in Figure 2, the set of curves corresponds to $E_{\sigma+\pi}$ between 20 kcal/mol (left) and 200 kcal/mol (right). Beyond $\Delta E_{ST} = {}^1/_4E_{\sigma+\pi}$, each curve splits since the trans-bent minimum has a positive force constant, while the planar saddle point has a negative one.

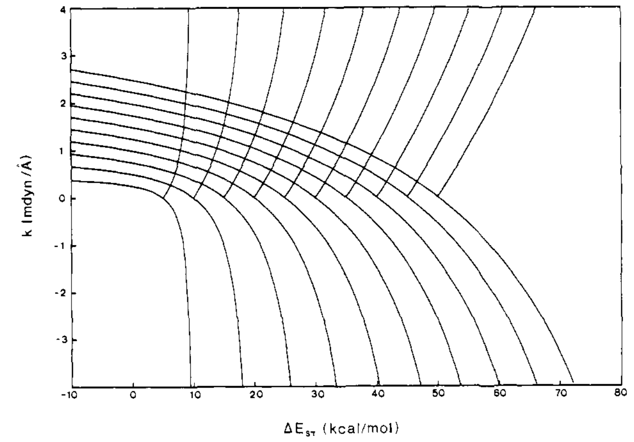

Figure 4. Enlargement of Figure 3 in a more realistic domain of validity and application of the model.

Conclusion

This analytical modelling uses rather crude assumptions; nevertheless, it yields a condition for trans bending which is similar to that obtained elsewhere with a qualitative valence bond approach. That work was based on a questionable avoided crossing

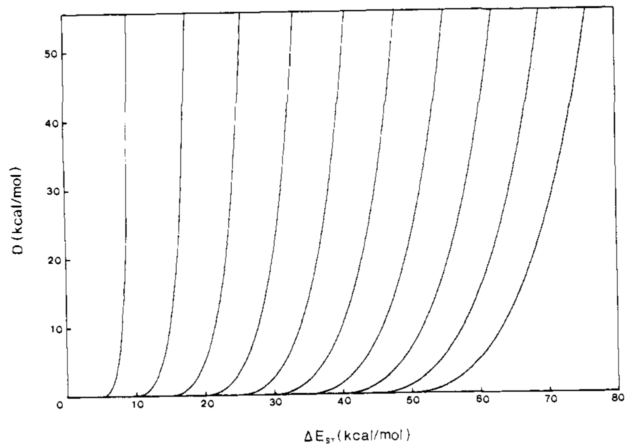

Figure 5. Barriers to planarity versus ΔE_{ST} as calculated from eq 20 for the set of $\sigma + \pi$ bond energies from 20 kcal/mol (left) to 200 kcal/mol (right).

hypothesis, but it proved to have some success in explaining and predicting nonclassical distortions.[1]

The present MO treatment provides further information which was not given by the previous VB model. It first defines the entire domain of existence of a double bond scheme, beyond which a direct X═X link no longer occurs. In addition, for trans-bent structures, the model provides simple analytical expressions to evaluate the trans-bending angle, the barrier to planarity, and the wagging force constant (this last index is also given for planar structures). The previous model was unable to predict these measurements of the *extent* of trans bending. A forthcoming paper will describe detailed orthogonal valence bond analyses and determine whether the avoided crossing hypothesis is valid or not.[6]

One might question the formulation in terms of ΔE_{ST} and $E_{\sigma+\pi}$ rather than moving back to fundamental atomic properties. This reductive operation is neither necessary nor straightforward since there exist contradictory trends between, for instance, the $(\epsilon_s - \epsilon_p)$ energy difference and the spatial properties of the atomic s and p orbitals.[25]

The semiquantitative success of such treatment may even be astonishing. It is likely that some error compensation fortuitously occurred among the three crudest approximations which are as follows: (1) neglecting overlap (which simplifies the MO spacing in Figure 1), (2) neglecting σ–π^* mixing, and (3) assimilating $(\epsilon_p - \epsilon_n)$ to ΔE_{ST}. In its present form, however, this modelization brings forward certain of the conditions required for good ab initio calculations (such as a correct ΔE_{ST} separation). It also provides simple rationalizations of unusual and sensitive phenomena affecting the structure of a whole family of double bonds and an elementary evaluation of their amplitude. More generally, it generates prospective ideas about overall conditions for bond building.

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Carboxylic Acid Participation in Amide Hydrolysis. Competition between Acid-Catalyzed Dehydration and Anhydride Formation

Ronald Kluger* and John C. Hunt

Contribution from the Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1. *Received December 27, 1988*

Abstract: The hydrolysis of 4′-methoxysuccinanilic acid in acidic solution proceeds via intramolecular catalysis, initially producing succinic anhydride and anisidine. The disappearance of the reactant is acid-catalyzed, but this is initially due to dehydration to produce an unstable equilibrium with 4′-methoxy-*N*-phenylsuccinimide. In contrast, the acid-catalyzed reaction of 4′-methoxymaleanilic acid does not produce an imide. In the case of the maleanilic acids, the low kinetic barrier to the formation of the hydrolysis products prevents the intermediate formation of an imide.

The rapid hydrolysis of amides through a reaction involving participation by a neighboring carboxylic acid is a reaction that has received attention as a model for enzymic catalysis.[1-5] Formation of addition intermediates of amides by a bimolecular reaction is subject to a high activation barrier[6,7] and reaction with the intramolecular carboxylic acid minimizes the entropic component of that process. After a carboxylic acid group adds to an amide to form a tetrahedral intermediate, elimination of the amine moiety produces an anhydride. Since the kinetic barrier to the hydrolysis of anhydrides is considerably lower than that for the hydrolysis of an amide, the intramolecular addition of a carboxyl group to the amide produces a catalytic route for hydrolysis.

In acidic solutions, the undissociated carboxylic acid form of an amic acid (an amic acid is a compound with neighboring amide and carboxyl groups) is the kinetically significant reaction species in the formation of the anhydride.[1-5] In less acidic solutions, the conjugate base of the amic acid predominates and the rate of reaction decreases. The slow hydrolysis may occur in competition with an initial dehydration to the corresponding imide,[8] especially where deprotonation on nitrogen can occur. Imide formation is also observed for reactions in nonaqueous solutions where dehydration is promoted.[8,9]

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