by water (^2H_2O) does not appear to be a major conformational determinant. It should be noted, however, that the agreement between NMR and MO data is not perfect, and that some contribution to preferred furanose geometry made by solvation is possible, especially for the α anomers **1** and **3**. As pointed out by a reviewer, the effect of water on preferred conformation cannot be convincingly settled without explicit consideration of water in either a quantum or statistical mechanics treatment.

Most interestingly, the ^1H–^1H and ^{13}C–^1H coupling data[6] obtained for β-D-erythrofuranose **2** was found to be insufficient to assign a preferred conformation in ^2H_2O. Indeed, as stated earlier,[6] **2** appears to assume more than one "stable" conformation in aqueous solution. The MO calculations, at least with the 3-21G basis set, support this conclusion. Angyal[24] has suggested, based on ^1H–^1H spin couplings, empirical observations and model inspection, that **2** interconverts between two conformers, namely, $^2T_3$ and $^3T_2$. These are the same conformers found to be most stable by MO calculations (Figure 10). Of the four ring configurations studied, β-D-erythrofuranose **2**, which is structurally related to the β-D-ribofuranose constituent of RNA, appears unique in several respects (see Figures 8, 9, and 10). Most notably, this structure can assume two relatively stable conformers, apparently similar to β-D-ribofuranose.[8a,23] It is not inconceivable that this configuration is the most energetically suitable for these biopolymers, being more able to assume significantly different "north" and "south" conformers (Figure 2) in order to accommodate a different polymer conformation required for a given biological process (i.e., RNA-protein binding).

Because of the uncertainties inherent in ab initio STO-3G MO calculations on "complex" molecules like **1–4**, the energy differences between conformers (Figure 10) cannot be considered quantitatively accurate. For example, STO-3G optimizations of **3** predict E_4 and E_3 to be the most and least stable *envelope* conformers, respectively, with an energy difference in 2.1 kcal/mol. Single-point calculations with the 3-21G basis set using STO-3G optimized molecular parameters indicate E_4 and E_0 to be most and least stable, respectively, with an energy difference of 3.9 kcal/mol; 3-21G geometry optimization increases this difference to 4.3 kcal/mol. The planar form of **3** is less stable than the envelope conformers, but the energy difference between it and the least stable envelope form is small (~0.3 kcal/mol). Thus, inversion cannot be excluded as a mechanism of conformer interconversion at room temperature. STO-3G optimizations and 3-21G single-point calculations do suggest that **2** and **3** interconvert between envelope conformers via pseudorotation more easily than **1** and **4**, but this conclusion requires validation from more sophisticated calculations.

The pseudorotational pathway[1,2] of interconversion of furanose conformers (Figure 2) assumes that adjacent envelope forms (e.g., E_2 and ^3E) interconvert via a twist form (i.e., ^3_2T). Implicit in the energy plots shown in Figure 10 is the assumption that a twist form will have an energy close to that of adjacent envelope forms; that is, these curves are smooth and continuous. We have not conducted optimizations on twist forms to verify this assumption in all cases. We have, however, conducted a calculation that supports this assumption. As shown in Table I and Figure 10, STO-3G calculations indicate that E_4 is the most stable envelope form of **3**. When the endocyclic torsion angle is allowed to relax from its E_4-constrained value of 0° and the structure is reoptimized, a new minimum energy conformer, $^0T_4$, is obtained with the structural parameters given in Table II. None of the bond lengths change appreciably. The largest changes are about 6° in several torsions, including that previously constrained to 0°. This "dissymmetric" twist form (see the legend for Figure 2) is only 0.1 and 0.2 kcal/mol lower in energy than E_4 and ^0E, respectively, as expected if pseudorotation is continuous. These results also indicate that while twist forms rather than envelope forms may be the true lowest energy conformers of **1**, **2** and **4**, very little energy is required to convert a twist form to neighboring envelope forms.

These ab initio studies have shown that furanose rings are dynamic structures not only with respect to bond torsions (i.e., pseudorotation, inversion) but also bond lengths and angles. The present study has identified general patterns that exist between furanose ring structural parameters, ring configuration, and ring conformation. The major findings are consistent with concluions derived from NMR coupling data, indicating that calculations such as these can provide useful information on the structural and dynamic behavior of furanose systems.

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Registry No. **1**, 72599-80-5; **2**, 72599-81-6; **3**, 80877-72-1; **4**, 80877-73-2.

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Nonclassical Distortions at Multiple Bonds

Georges Trinquier* and Jean-Paul Malrieu

Contribution from the Laboratoire de Physique Quantique (C.N.R.S., U.A. No. 505), Université Paul-Sabatier, 31062 Toulouse Cedex, France. *Received November 26, 1986*

Abstract: Both experiments and ab initio calculations exhibit cases where double bonds deviate from planarity, and cumulenones or triple bonds deviate from linearity. In a simple valence bond modelling, the occurrence and extent of these distortions are related to the singlet–triplet separation ($\Delta E_{S\rightarrow T}$) of the interacting fragments forming the multiple bond. This explains why inclusion of electron correlation may be so crucial for a reliable description of such deformations through quantum calculations. Various distortions are explained and others suggested for a set of unsaturated systems including alkynes, olefins, ketenes, cumulenes, allenes, ylides, and diazo compounds whenever they are built from fragments with a large $\Delta E_{S\rightarrow T}$. Possible extensions to transition metal complexes are proposed.

Trans-bent distortions of double bonds occur in two types of strain-free unsaturated systems. The first type is the pseudoolefins $H_2X{=}XH_2$, X being a heavier analogue of carbon, i.e., Si, Ge, and Sn. According to accurate ab initio calculations, the deviation from planarity, **1**, increases from $\theta = 0°$ for carbon, to $\theta = 40°$ for germanium or tin.[1,2] Disilene, $H_2Si{=}SiH_2$, is on the bor-

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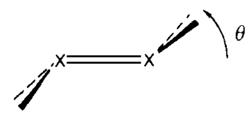
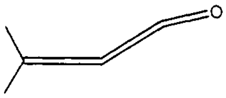


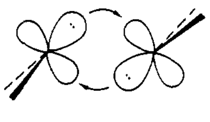
1

derline, the bending angle depending on the accuracy of the calculation.[3] The second type of distortion concerns the nonlinearity of cumulenones. Propadienone, $H_2C{=}C{=}C{=}O$, exhibits a striking trans-bent deformation **2** according to experimental data[4] and ab initio calculations including electron correlation.[5a] The zigzag shape has been evidenced on longer analogues and suggested to be a general feature in the series.[5b,c]



2

The electronic structures of the former unusual "double" bonds have been rationalized in terms of dative bent bonds between two ground-state singlet carbene analogues.[1,2a,6] The electrons of one n_σ lone pair delocalize into the empty p_π atomic orbital (AO) of the neighboring fragment, **3**. This simple explanation can be extended to the cumulenone problem, **4**, where one of the two orthogonal conjugations is basically independent of the bending angle (the AO's of this invariant π system are now shown in **4**).



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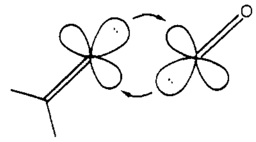

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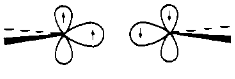
The deviation from planarity of ethylene analogues was shown to depend on the singlet–triplet separation $\Delta E_{S\to T}$ of the carbene-like fragments.[2a] When their singlet configuration is much more stable than their triplet configuration, the formation of a classical planar $\sigma + \pi$ double bond, which requires the interaction of triplet states, **5**,[7] becomes impossible. The bent arrangement brings about a certain electron delocalization from the ground singlet state of the fragments. This statement is also valid for propadienone since both CO and $H_2C{=}C$ have large $\Delta E_{S\to T}$ separations (139 and 46 kcal/mol, respectively).[8]



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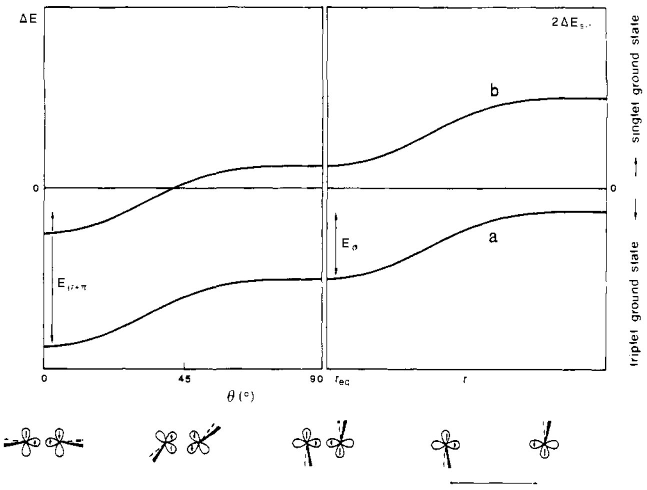

Figure 1. Schematic energy profile for the coupling of two triplet carbenes to form an olefin. Zero energy refers to two separated singlet carbenes: (a) triplet ground states, (b) singlet ground states.

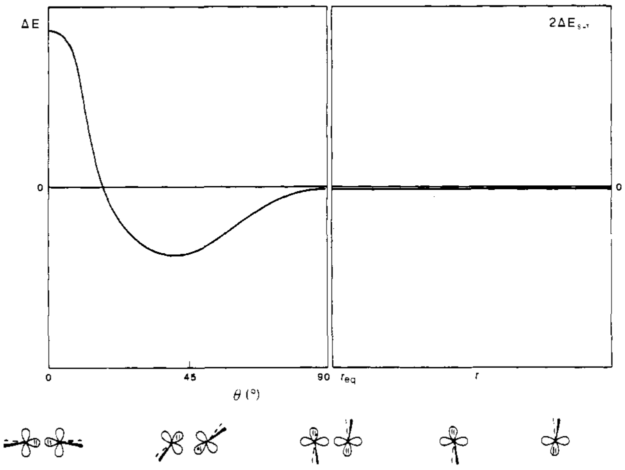

Figure 2. Schematic energy profile for the coupling of two singlet carbenes into an excited olefin.

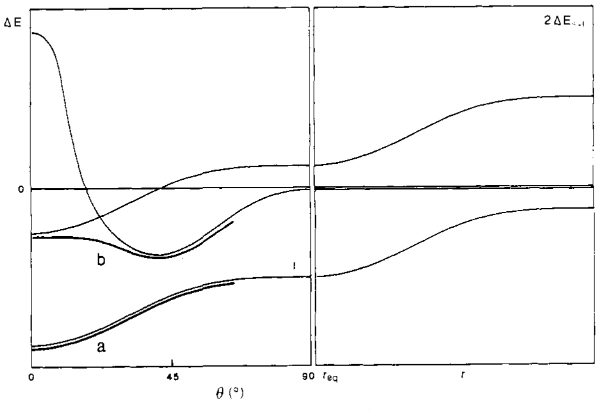

Figure 3. Superimposition of Figures 1 and 2 with the resulting possible mixing.

The present paper proposes a simple modelling for these nonclassical distortions at double bonds in terms of singlet–triplet

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[1] (a) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268. (b) Cotton, J. D.; Davidson, P. J.; Lappert, M. F.; Donaldson, J. D.; Silver, J. *Ibid.* **1976**, 2286.

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[3] (a) Krogh-Jespersen, K. *J. Phys. Chem.* **1982**, *86*, 1492. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (c) Olbrich, G. *Chem. Phys. Lett.* **1986**, *130*, 115. (d) Somasundran, K.; Amos, R. D.; Handy, N. C. *Theor. Chim. Acta* **1986**, *70*, 393.

[4] (a) Brown, R. D.; Godfrey, P. D.; Champion, R.; McNaughton, D. *J. Am. Chem. Soc.* **1981**, *103*, 5711. (b) Brown, R. D.; Champion, R.; Elmes, P. S.; Godfrey, P. D. *Ibid.* **1985**, *107*, 4109.

[5] (a) Farnell, L.; Radom, L. *Chem. Phys. Lett.* **1982**, *91*, 373. (b) Farnell, L.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 25. (c) Brown, R. D.; Godfrey, P. D.; Ball, M. J.; Godfrey, S.; McNaughton, D.; Rodler, M.; Kleibömer, B.; Champion, R. *Ibid.* **1986**, *108*, 6534.

[6] See also less straight arguments: Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 3871.

[7] The building of ethylene from two triplet methylenes has been noticed for a long time; see, for instance: (a) Cheung, L. M.; Sundberg, K. R.; Ruedenberg, K. *J. Am. Chem. Soc.* **1978**, *100*, 8024. (b) Bernardi, F.; Robb, M. A. *Mol. Phys.* **1983**, *48*, 1345.

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

separation of the fragments. On this basis, both rationalizations of structural data from the literature and suggestions for potential structural distortions will emerge for a series of unsaturated compounds. Recently, Carter and Goddard suggested a simple correlation between the *strength* of typical $\sigma + \pi$ *planar* double bonds and the $\Delta E_{S\to T}$ of their fragments.[9] Our contribution may be considered as a *structural* extension of this kind of argument to the occurrence of nonplanar (or nonlinear) minima on potential surfaces.

In the modelling section, we chose to use valence bond arguments which here we think are simpler and more powerful than pure molecular orbital (MO) considerations. Because trans-bent distorsions in pseudoolefins can be accounted for by MO arguments as well, in Appendix I we propose a one-electron MO analysis of trans-bent distortions in pseudoolefins.

Classical vs. Nonclassical Double Bonds

A. Modelling with Simple Carbenes XH_2. In a valence bond approach (developed in Appendix II), let us consider the energy of two limiting wave functions: one built from the coupling of two triplet fragments, the other from the coupling of two singlet fragments. Their possible mixing, resulting in tiny energy changes (see Appendix II), is neglected at first. The only coplanar coupling of the two carbene-like species would be relevant only for the study of the strength of a planar $\sigma + \pi$ double bond. For a structural analysis, it is necessary to study the influence of both the distance r between the fragments and their bending (or wagging) angle θ. The two species are first brought to a relevant distance in an orthogonal bent geometry (step 1), then recover planarity through trans-wagging (step 2), the whole motion keeping a C_{2h} symmetry, **6**.

6

The energy variation when the two carbene groups are in their triplet state is displayed in Figure 1, where the zero of energy corresponds to the separated pair of *singlet* configurations. Curves a and b picture triplet ground-state ($\Delta E_{S\to T} < 0$) and singlet ground-state ($\Delta E_{S\to T} > 0$) species, respectively. The first step (Figure 1, right) basically creates a σ bond (of energy E_σ), while the second step (Figure 1, left) leads to the construction of a typical $\sigma + \pi$ double bond (of energy $E_{\sigma+\pi}$). The resulting relative energy (top left) corresponds to the olefin bond energy

$$D = 2\Delta E_{S\to T} - E_{\sigma+\pi}$$

The major role of the singlet–triplet separation, clearly shown in Figure 1, has been discussed by Carter and Goddard in their study of the coplanar coupling of two triplet carbenes.[9]

Figure 2 pictures the coupling of two singlet carbenoids. Step 1 (right) does not create any bond while keeping the repulsion negligible due to the trans arrangement and to the nonoccupancy of the p_π AO's in the singlet moieties. Step 2 first authorizes some electronic delocalization from the σ lone pairs to the empty p_π AO of the partner (through two dative bent bonds). This effect is maximum in the region of $\theta \simeq 45°$. For smaller angles the repulsion prevails since at $\theta = 0°$ the two lone pairs strongly repel each other without any electron delocalization. So, if the fragments keep a singlet electronic structure, the "double" bond takes up a trans-bent conformation.

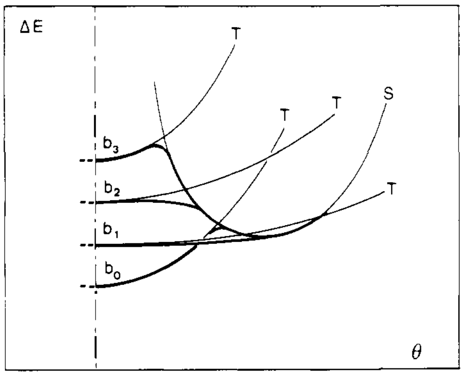

Figure 4. Various shapes for singlet–singlet and triplet–triplet curve crossing.

Figure 3 is a superimposition of Figures 1 and 2. In curve a (triplet ground-state fragments) the molecular ground state keeps a triplet content without significant mixing with the singlet pairing, so the planar structure, corresponding to a classical $\sigma + \pi$ double bond, definitely prevails. In curve b, a crossing between the triplet pair and the singlet pair occurs giving two symmetrical trans-bent minima on the potential surface, with the planar form ($\theta = 0°$) being a saddle point. Depending on the relative position of the two curves and on the extent of mixing, different shapes can be encountered for the resulting curve. Some of these are displayed in Figure 4. Among them, case b_1 is noteworthy; it corresponds to a very flat shape to be associated with a weak wagging force constant. The competition between the triplet–triplet and singlet–singlet potential surfaces explains the existence of planar or trans-bent equilibrium structure, but the mixing between these diabatic states will result in quantitative effects: for planar compounds, the existence of a low-lying singlet–singlet potential surface will lead to a weak wagging force constant, while for bent compounds the bending angle will be more pronounced when the triplet–triplet potential surface lies higher in energy than when their separation is weak. These quantitative trends will be verified several times in the forthcoming examples.

The depth of the singlet–singlet potential well is estimated in Appendix II to be approximately half of an intrinsic classical $\sigma + \pi$ bond energy. Case b_1 occurs therefore when

$$\Sigma\Delta E_{S\to T} \simeq {}^1\!/_2 E_{\sigma+\pi} \qquad (1)$$

and case b_2 (trans-bent absolute minimum) should be observed when

$$\Sigma\Delta E_{S\to T} > {}^1\!/_2 E_{\sigma+\pi} \qquad (2)$$

B. Confrontation to Structural Results. We would first like to point out a technical requirement in quantum calculations of structures. Since the structure is governed by $\Delta E_{S\to T}$ of the fragments (see Figure 3), the reliability of a predicted equilibrium structure strongly depends on the accuracy of this energy gap. A correct $\Delta E_{S\to T}$ gap is only obtained when the radial and angular correlation of the n_σ singlet lone pair is taken into account. One understands therefore that the uncorrelated molecular treatment, underestimating the $\Delta E_{S\to T}$ separation, may miss the trans-bent minimum which only reappears when correlation is included. Examples are provided with $H_2Si{=}SiH_2$[3a] and H_2CCCO.[5a]

In the $H_2X{=}XH_2$ series of group 14, ethylene is known to be planar and clearly belongs to case a of Figure 3 ($\Delta E_{S\to T} \simeq -10$ kcal/mol). Silylene, SiH_2, has a $\Delta E_{S\to T}$ of 19 kcal/mol[8] which gives $\Sigma\Delta E_{S\to T} = 38$ kcal/mol. A mean value of ${}^1\!/_2 E_{\sigma+\pi}$ for Si=Si can be taken at 37 kcal/mol from ref 10. Condition 1 is therefore satisfied, and disilene should have a very flat potential curve (case b_1). Calculations actually do lead to this conclusion, as summarized by Raabe and Michl: "Disilene is effectively planar in that the planar geometry and geometries pyramidalized on silicon

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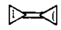
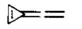
[9] Carter, E. A.; Goddard, W. A., III *J. Phys. Chem.* **1986**, *90*, 998.

[10] Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

Table I. Application of Condition 2′ to Some Olefinic and Allenic Systems[a]

	$f(E_{\sigma+\pi})$	$\Sigma\Delta E_{S\rightarrow T}$	expected structure
$H_2C{=}CH_2$	86	−20	P
$H_2C{=}SiH_2$	52–56	9	P
$H_2C{=}GeH_2$	45–52	12.5	P
$H_2Si{=}SiH_2$	37	38	NP
$H_2Ge{=}GeH_2$	32	45	NP
$H_2Sn{=}SnH_2$	30–32	45	NP
$H_2C{=}CF_2$	97	40	P
$F_2C{=}CF_2$	120	100	P
$H_2C{=}SiF_2$	57–61	63	NP
$F_2C{=}SiH_2$	59–63	69	NP
$F_2C{=}SiF_2$	71–76	123	NP
$H_2C{=}GeF_2$	48–56	64	NP
$F_2C{=}GeH_2$	51–59	72.5	NP
$F_2C{=}GeF_2$	61–70	124	NP
$F_2Si{=}SiF_2$	48	146	NP
$F_2Ge{=}GeF_2$	42	148	NP
	145	100–120	P[b]
$H_2C{=}C{=}CH_2$	86	36	L
$F_2C{=}C{=}CH_2$	97	96	L
$H_2Si{=}C{=}CH_2$	52–56	65	NL
$H_2C{=}Si{=}CH_2$	52–56	30–50	L
$F_2C{=}Si{=}CH_2$	59–64	90–110	NL
	102	96–106	P[b]

[a] All energies are given in kcal/mol. $f(E_{\sigma+\pi}) = {}^1/_2E_{\sigma+\pi}[1 + (q_1 + q_2)/2] + 200q_1q_2$. q_1 and q_2 are the possible π net charges on the two carbene centers forming the double bond. When $f(E_{\sigma+\pi})$ is smaller than $\Sigma\Delta E_{S\rightarrow T}$ (the sum of the singlet–triplet separations for the two fragments) the system is expected to be nonplanar (NP) or nonlinear (NL); otherwise it is expected to be planar (P) or linear (L). The $\Delta E_{S\rightarrow T}$ are taken from ref 8; otherwise the following values were taken: GeH_2, 22.5 (ref 11); SnH_2, 22.5 (ref 12); SiF_2, 73 (ref 17); GeF_2, 74 (ref 21); H_2CSi, 40–60. The bond energies $E_{\sigma+\pi}$ were taken as follows: C=C, 172 (ref 9); Si=C, 105 (ref 10)–113 (ref (3b); Ge=C, 90–105; Si=Si, 74 (ref 10); Ge=Ge, 65 (ref 10); Sn=Sn, 60–65. The π net charges were obtained from ab initio calculations: CF_2, 0.25; SiF_2, 0.16; GeF_2, 0.15; C_3H_2, 0.37. [b] Cases where π conjugation should increase the value of $E_{\sigma+\pi}$ thus favoring planarity.

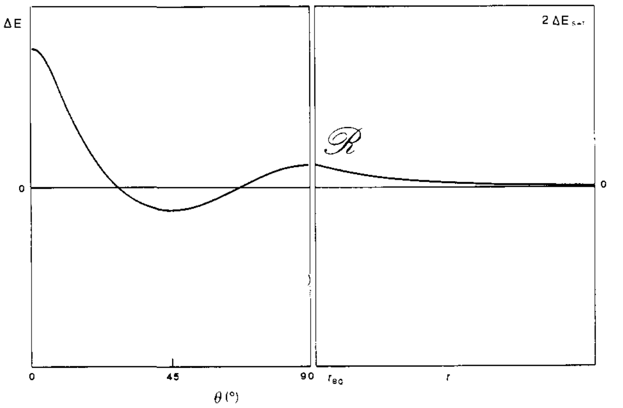


Figure 5. Schematic energy profile for the coupling of two singlet carbenes bearing π-donor substituents.

up to quite large angles (20°) are essentially equal in energy within 1 or 2 kcal/mol."[3b] Germylene, GeH_2, has a $\Delta E_{S\rightarrow T}$ of 22.5 kcal/mol[11] which gives $\Sigma\Delta E_{S\rightarrow T} = 45$ kcal/mol. If we take a mean value of 32 kcal/mol as ${}^1/_2E_{\sigma+\pi}$ for Ge=Ge,[10] then condition 2 is satisfied and $H_2Ge{=}GeH_2$ should correspond to case b_2 of Figure 4 (or b of Figure 3). Digermene is actually found to be trans-bent at both the SCF and CI levels of calculation.[2a] Accurate calculations predicted a $\Delta E_{S\rightarrow T}$ separation in SnH_2 at 22.5 kcal/mol.[12] Since the Sn=Sn double bond should be weaker than the Ge=Ge one, it is easy to understand the nonplanar structure observed for distannene which is bent slightly more than that for digermene.[1]

Table II. SCF-DZ Results on Cyclopropenylidene and Triafulvalene

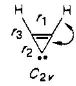
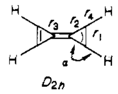
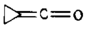
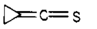
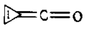
	$r_1 = 1.327$ Å $r_2 = 1.441$ Å $r_3 = 1.072$ Å $\alpha = 148.5°$
	$r_1 = 1.313$ $r_2 = 1.471$ $r_3 = 1.307$ $r_4 = 1.072$ $\alpha = 147.9$
$\Delta E^{SCF}(2C_3H_2 \rightarrow C_6H_4)$	−44.5 kcal/mol

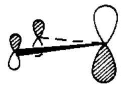
Table III. Application of Condition 2″ to Some Ketene and Cumulenone Systems and Their Thio Analogues[a]

	$f(E_{\sigma+\pi})$	$\Sigma\Delta E_{S\rightarrow T}$	expected structure
$H_2C{=}C{=}C{=}O$	146	185	NL
$H_2C{=}C{=}C{=}S$	140–144	125	L
$O{=}C{=}C{=}C{=}O$	146	152	NL
$S{=}C{=}C{=}C{=}S$	140–144	84–94	L
$H_2C{=}C{=}O$	146	129	P
$H_2C{=}C{=}S$	140–144	69	P
$F_2C{=}C{=}O$	192	189	P
	146	145–150	NP
	140–144	85–90	P
	213	190–200	P
$H_2Si{=}C{=}O$	89–96	158	NP
$H_2Si{=}C{=}S$	85–95	98	NP
$H_2C{=}Si{=}O$	85–95	86	P
$H_2C{=}Si{=}S$	85–95	76	P
$F_2C{=}Si{=}O$	114–133	146	NP
$F_2C{=}Si{=}S$	114–133	136	NP
$H_2N^+{=}C{=}O$	115–125	109	P
$H_2P^+{=}C{=}O$	95	155	NP

[a] All energies are given in kcal/mol. $f(E_{\sigma+\pi}) = E_{\sigma+\pi}[{}^3/_4 + (q_1 + q_2)/8] + 200q_1q_2$. This table reads as Table I. When not defined in Table I, the numerical parameters were taken as follows. $\Delta E_{S\rightarrow T}$: CS, 79 (ref 25); SiO, 96 (ref 25); SiS, 86 (ref 25); C_3H_4, 6–11 (ref 8); CCO, 13 (see footnote 28); CCS, 5–15 (estimate). Bond energies $E_{\sigma+\pi}$: N=C, 135 (ref 10)–147 (ref 26); P=C, 112 (ref 10). π net charges: CO, 0.8; CS, SiO; SiS, 0.5–0.7.

Heteroatomic double bonds $H_2X{=}YH_2$ may be analyzed with the same criteria. Neither $H_2Si{=}CH_2$ ($\Sigma\Delta E_{S\rightarrow T} = 9$ kcal/mol) nor $H_2Ge{=}CH_2$ ($\Sigma\Delta E_{S\rightarrow T} = 12$ kcal/mol) should deviate from planarity, but the question is open regarding $H_2Si{=}GeH_2$ since $\Sigma\Delta E_{S\rightarrow T}$ (=42 kcal/mol) is of the order of magnitude of a Si—Ge σ-bond energy. The same comment applies to $H_2Si{=}SnH_2$ as well. The case of $H_2Ge{=}SnH_2$ is close to those of digermene or distannene and should also be trans-bent.

C. Refinements for π-Conjugated Carbenes. When the carbene bears π-donor substituents such as in CF_2, the p_π AO which was empty in the previous treatment is now partly occupied owing to the donation of π lone pairs of the substituents (F, NR_2, etc.).[13] The carbon region should therefore induce a more isotropic repulsion, thus a lesser distorsion. On the other hand, the delocalization of the n_σ pair into this p_π orbital, which is, in fact, a π^* MO with a strong coefficient on carbon, **7**, should be smaller,



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resulting in a reduced depth of the singlet–singlet potential well. Consequently, the coupling of two singlet carbenes should have

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(11) Phillips, R. A.; Buenker, R. J.; Beardsworth, R.; Bunker, P. R.; Jensen, P.; Kraemer, W. P. *Chem. Phys. Lett.* **1985**, *118*, 60.

(12) Balasubramanian, K. *Chem. Phys. Lett.* **1986**, *127*, 585.

(13) Hyperconjugation may also contribute to the population of the p_π orbital but to a lesser extent. We shall neglect this effect all along this work.

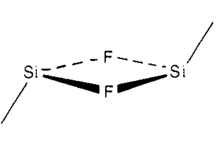
a different shape. First, in step 1 of coupling **6**, the energy curve (Figure 2, right-hand part) should now be repulsive owing to the repulsion of the net charges in the p_π orbitals. At the equilibrium distance, a repulsion energy $\mathcal{R}$ is lost, which can be approximated (see Appendix II.c) by $\alpha q_1 q_2$ (q_1 and q_2 being the π net charges on the carbene centers; α is a proportionality factor that will be defined further on). Second, the depth of the potential well (left-hand part of Figure 2) should be reduced so that the shape of the whole couplings of two singlets bearing p_π net charges is that given in Figure 5. In Appendix II.c we show that the depth of the potential well can in this case be approximated by $^1/_2 E_{\sigma+\pi}[1 - (q_1+q_2)/2]$. So, when q_1 and q_2 are the net charges of the p_π orbitals, condition 2 now becomes condition 2′:

$$\Sigma\Delta E_{\mathrm{S}\to\mathrm{T}} > \frac{1}{2}E_{\sigma+\pi}\left(1 + \frac{q_1 + q_2}{2}\right) + \alpha q_1 q_2 \qquad (2')$$

The proportionality factor α can be estimated from a simple calculation of the $(\pi \to \sigma^*)^2$ excitation energy in ethylene. This leads to $\alpha = 212$ kcal/mol.[14] However, we shall take $\alpha = 200$ kcal/mol, a universal factor which seems to fit the whole series of comparisons.

Let us examine the case of tetrafluoroethylene. The π net charge on the carbon atom in difluorocarbene CF_2 has been calculated at 0.25 e. The right-hand side of condition 2′, which we shall call $f(E_{\sigma+\pi})$, is then 120 kcal/mol (taking $E_{\sigma+\pi}$ for the C=C bond to be 172 kcal/mol as recommended in ref 9), while $\Sigma\Delta E_{\mathrm{S}\to\mathrm{T}}$ is only 100 kcal/mol (taking $\Delta E_{\mathrm{S}\to\mathrm{T}}$ in CF_2 to be 50 kcal/mol).[8] So, condition 2′ is not satisfied, and $F_2C{=}CF_2$ remains planar though its wagging force constant is expected to be significantly lower than that of ethylene.

For fluorinated substituted pseudoolefins containing Si or Ge, condition 2′ is satisfied either for the 1,1-fluorinated derivatives or for the 1,1,2,2-fluorinated derivatives, as can be seen in Table I. SiF_2 has a large $\Delta E_{\mathrm{S}\to\mathrm{T}}$ (73 kcal/mol)[17] and the molecule $F_2Si{=}SiF_2$ should be trans-bent. Calculations have shown that its energy decreases when going from planar to trans-bent geometry,[18] but the molecule then breaks its Si=Si link and adopts a strongly polar, doubly bridged structure, **8**.[19] The same trends are observed for $(GeF_2)_2$,[20] which fits with the large $\Delta E_{\mathrm{S}\to\mathrm{T}}$ calculated for GeF_2 (74 kcal/mol).[21] $H_2Si{=}CF_2$ ($\Sigma\Delta E_{\mathrm{S}\to\mathrm{T}}$ = 69 kcal/mol) might be slightly distorted. $F_2Si{=}CF_2$ ($\Sigma\Delta E_{\mathrm{S}\to\mathrm{T}}$ = 123 kcal/mol)[8,17] should be either trans-bent or doubly bridged. $H_2Ge{=}CF_2$ ($\Sigma\Delta E_{\mathrm{S}\to\mathrm{T}}$ = 72.5 kcal/mol) should be nonplanar. like $H_2Si{=}CF_2$ and $H_2Sn{=}CF_2$. The mixed pseudoolefins $F_2X{=}YF_2$, with X, Y = Si, Ge, Sn, which are not shown in Table I, should have, like Si_2F_4 and Ge_2F_4, a doubly bridged structure since they all show a very large difference between the two sides of relation 2′.

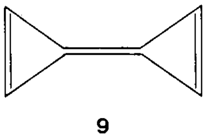


8

Planar structures have been reported for all mono- and difluorosilaethylenes,[22] but these were optimized at the SCF level and, most likely, under a planarity constraint. Refinements such as release of planar constraints and inclusion of correlation effects would be required to settle the problem.

Amino substitution has about the same effect on $\Delta E_{\mathrm{S}\to\mathrm{T}}$ as fluorine substitution ($\Delta E_{\mathrm{S}\to\mathrm{T}}$ = 50 kcal/mol for $C(NH_2)_2$).[8] However, a larger p_π net charge might occur owing to the enhanced donor property of the amino lone pair. For this reason we are not sure that for amino-substituted olefins we can infer the same conclusions as those obtained for fluoro-substituted olefins.

The case of triafulvalene (or dicyclopropenylidene), **9**, gives a typical illustration of the crucial role of p_π partial occupation in preventing distortion. Because of the aromatic character of its π system, each cyclopropenylidene fragment has a large singlet–triplet separation, and a large π net charge on the carbene center, which as been calculated at 0.37 e at the SCF–DZ level.[23] As shown in Table I, condition 2′ is not satisfied and the molecule is expected to be planar even without taking into account π delocalization. In fact, because of pure π conjugation in **9**, the coupling of two triplet cyclopropenylidenes brings not only the typical $E_{\sigma+\pi}$ but also an extra π conjugation energy, evaluated at 1.9β from simple topological π Huckel arguments. This effect further favors planarity in **9**. SCF calculations performed with a DZ basis set actually lead to a planar D_{2h} geometry whose parameters are given in Table II. We have checked that any C_{2h} distortion results in an energy increase.



9

Replacing a methylene fragment of the olefin by a valence isoelectronic parent should lead to similar analyses despite the lesser symmetry for N-H, P-H, N-F or P-F. The geometrical problem is the same with the ions PR_2^+ and NR_2^+. The ion $H_2Si{=}PF_2^+$, for instance, should be highly distorted since $\Delta E_{\mathrm{S}\to\mathrm{T}}$ for PF_2^+ is about 84 kcal/mol.[8]

Generalizations

A series of extensions to less typical double bonds or triple bonds are proposed in the present section.

A. Cumulenones. Propadienone may be considered as being built from two fragments: a vinylidene and a carbonyl (see **4**) which both have a singlet ground state ($\Delta E_{\mathrm{S}\to\mathrm{T}}$ = 46 and 139 kcal/mol, respectively). The observed trans-bent distortion of propadienone or higher cumulenones may be understood as a compromise to keep the singlet nature of the fragments while maintaining the conjugation between the two bonds. However, neither condition 2 nor condition 2′ should be considered directly when the CO fragment is involved. The p_π AO of the carbon atom in the CO group is largely occupied, resulting in an enhanced isotropic repulsion of the carbon region. This explains the rather weak deviations from linearity observed in the C=C=O frames (at most ≈10°). The estimation of the singlet–singlet potential well must therefore proceed on the basis of a linear C–C–O arrangement **10**. In Appendix II.d, we have estimated the depth of this well to be $E_{\sigma+\pi}[^1/_4 - (q_1 + q_2)/8]$, with q_1 and q_2 being the π net charges of the p_π orbitals of the carbene center and of the carbonyl group (or thiocarbonyl group, as we shall generalize),

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(14) See footnotes 23 and 34 for details on the methods of calculation. The experimental geometry of ethylene is taken from ref 15.

(15) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619.

(16) (a) Kenney, J. W.; Simons, J.; Purvis, G. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 6930. (b) Saxe, P.; Schaefer, H. F., III *Ibid.* **1980**, *102*, 3239.

(17) Colvin, M. E.; Grev, R. S.; Schaefer, H. F., III; Bicerano, J. *Chem. Phys. Lett.* **1983**, *99*, 399.

(18) Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1985**, *107*, 537.

(19) Saint-Roch, B.; Barthelat, J. C., unpublished theoretical result.

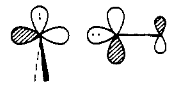
(20) Huber, H.; Kündig, E. P.; Ozin, G. A.; Vandervoet, A. *Can. J. Chem.* **1974**, *52*, 95.

(21) Barthelat, J. C., Saint-Roch, B.; Trinquier, G.; Satge, J. *J. Am. Chem. Soc.* **1980**, *102*, 4080.

(22) Gordon, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 4352.

(23) The SCF calculations were performed with the PSHONDOG program[24a] which results from the inclusion of pseudopotentials[24b] in the version of HONDO which contains the analytical calculation of the energy gradient.[24c] DZ refers to the use of a double-ζ basis set. DZd refers to the use of a double-ζ + d basis set. The d exponents were taken at 0.7, 1.25, and 0.45 for C, O, and Si, respectively (note that the DZd basis set does not include any d polarization orbitals on fluorine). The optimized geometries have gradient components lower than 0.0001.

(24) (a) Daudey, J. P.; Komiha, N., private communication. (b) Durand, Ph.; Barthelat, J. C. *Theor. Chim. Acta* **1975**, *38*, 283. (c) Dupuis, M.; King, H. F. *J. Chem. Phys.* **1978**, *68*, 3998.



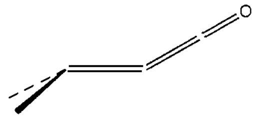
10

respectively. So, when a carbonyl group CO or a thiocarbonyl group CS is involved in the multiple bond, the previously defined condition 2′ is now changed into condition 2″ as follows:

$$\Sigma\Delta E_{S\to T} > E_{\sigma+\pi}\left(\frac{3}{4} + \frac{q_1+q_2}{8}\right) + \alpha q_1 q_2 \qquad (2'')$$

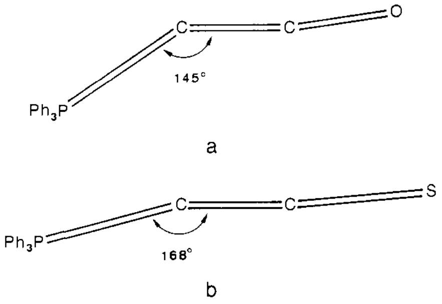
In Table III this relation is tested on a series of compounds containing a CO group or a CS group. The π net charge on the carbon of CO has been taken to 0.8 e, a realistic value which is larger than that obtained from an SCF calculation (with a DZ basis set we get only 0.6 e), but SCF wave functions are known to overestimate the C^+–^-O polarity in CO.[27] Condition 2″ is satisfied for $H_2C{=}C{=}C{=}O$ which is actually trans-bent, and not satisfied for $H_2C{=}C{=}O$ which is indeed planar (see next section), or for $H_2C{=}C{=}C{=}S$ which is expected to be linear.[62]

From our criteria, one also understands why distortion **11** does not occur in propadienone; the fragments involved in this distortion are CH_2 and $C{=}C{=}O$. Taking 13 kcal/mol as $\Delta E_{S\to T}$ in $C{=}C{=}O$,[28] $\Sigma\Delta E_{S\to T}$ remains very weak since $\Delta E_{S\to T} = -10$ kcal/mol for CH_2.



11

Phosphoranylideneketenes or thioketenes are particular cumulenones. The structures of $Ph_3P{=}C{=}C{=}O$ and $Ph_3P{=}C{=}C{=}S$ are known to be bent from X-ray studies performed in the midsixties.[29] The observed deviation from linearity happens to be larger in the former than in the latter, **12**, which is in line with the $\Delta E_{S\to T}$ separations of CO (139 kcal/mol) and CS (79 kcal/mol).[25] The departures from linearity are made clear when considering $Ph_3P{=}C$ as a special unsaturated carbene, **13**, which should have a large $\Delta E_{S\to T}$ owing to mixing of the occupied p_π AO with a d orbital on phosphorus and hyperconjugation of the empty p_π with a π-type occupied MO on the PH_3 group.



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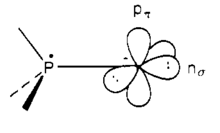
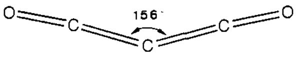


13

Carbon suboxide, C_3O_2, is another peculiar cumulenone which is known to be bent, **14**, both from spectroscopic measurements[30a,b] and from SCF ab initio calculations.[30c] C_3O_2 can be divided into OC + CCO in two equivalent ways which happen to induce the same bending on the central carbon atom, **15**. Condition 2″ is satisfied as can be seen in Table III. The two bending effects cumulate on the same carbon atom, and the observed bent structure is therefore accounted for.[30a–c] The results obtained for carbon subsulfide, $S{=}C{=}C{=}C{=}S$, is noteworthy. In spite of uncertainties for the parameters in (2″), $S{=}C{=}C{=}C{=}S$ is definitely expected to be linear (see Table III) and has actually been found to be linear by laser-excited phosphorescence spectroscopy.[30d] Tricarbon oxide sulfide, $O{=}C{=}C{=}C{=}S$, is known to be linear.[31] Applications of relation 2″ gives $\Sigma\Delta E_{S\to T} > f(E_{\sigma+\pi})$ for the oxide end (144–154 > 146) and $\Sigma\Delta E_{S\to T} < f(E_{\sigma+\pi})$ for the sulfide end (92 < 140–144). Since there is here no cumulative effect on the central carbon, these results can be seen as in agreement with the observed linear geometry.



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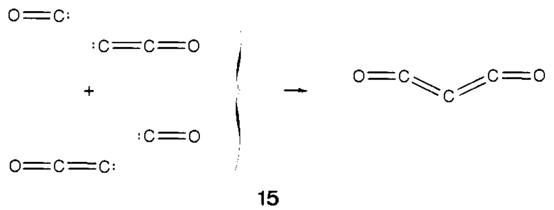

15

The cumulenone distortion should always occur since the unsaturated carbene part which is beside the CO group has always a significant $\Delta E_{S\to T}$.[16a] $H_2C{=}C{=}C$:, for instance, has a $\Delta E_{S\to T}$ of about 33 kcal/mol[16b] which satisfies condition 2″ in butatrienone.

A general feature of the cumulenone distortion is that the significant bending occurs necessarily at the β carbon atom (with respect to the terminal oxygen atom) since the only partitioning of the chain which ensures a large $\Sigma\Delta E_{S\to T}$ is that dividing off the CO fragment. The expected distorted geometries are planar bent, **16a**, or orthogonal bent, **16b**, according to whether the number n of inner carbon atoms of the chain $H_2C{=}(C)_n{=}O$ is even or odd, respectively, as noticed by Farnell and Radom.[5b] These authors calculated the barrier to planarity in butatrienone at 433 cm^{-1} by MP3/6-31G calculations, including correlation effects.[5b] Recently this work has been questioned and the barrier has been reevaluated at 6 cm^{-1} from SCF 6-31G** calculations.[5c]

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(25) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand-Reinhold: New York, 1979.

(26) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Interscience: New York, 1972.

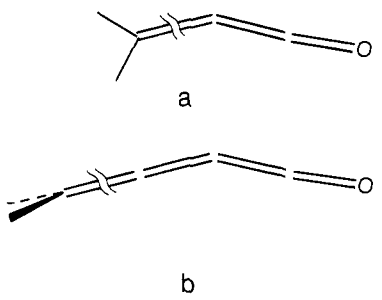
(27) Karafiloglou, P.; Malrieu, J. P. *Chem. Phys.* **1986**, *104*, 383.

(28) (a) The highest occupied MO level in linear :C=C=O is a doubly occupied degenerate π level. Consequently, the low-lying states are necessarily $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$, respectively, but they all correspond to a n_σ^2 configuration of the two carbenic electrons. The first state with a $n_\sigma p_\pi$ configuration is a $^3\Pi_i$ state. The relevant transition which would correspond to $\Delta E_{S\to T}$ could be the $^3\Sigma^-$ – $^3\Pi_i$ separation of 34 kcal/mol.[28b] However, because of the π configuration in $^3\Sigma^-$ (in which there are three electrons in π_x plus three electrons in π_y), a large π net charge is expected in the carbene p_π orbital, which is uneasy to evaluate. A more relevant starting point for the n_σ^2 configuration would be a x^2y^4 configuration, corresponding to the mixing of one component of $^1\Delta$ $(x^2y^2(x^2 - y^2))$ with $^1\Sigma^+$ $(x^2y^2(x^2 + y^2))$. This combination leaves the carbene $p_{\pi x}$ orbital empty. It can be located in mid distance between $^1\Delta$ and $^1\Sigma^+$, lying at 17 and 25 kcal/mol, respectively, above the $^2\Sigma^-$ ground state.[28b] Therefore, for :C=C=O we shall take $\Delta E_{S\to T} = 13$ kcal/mol and a π net charge $q = 0$. (b) Chabalowski, C. F.; Buenker, R. J.; Peyerimhoff, S. D. *J. Chem. Phys.* **1986**, *84*, 268.

(29) (a) Daly, J. J.; Wheatley, P. J. *J. Chem. Soc. A* **1966**, 1703. (b) Daly, J. J. *Ibid.* **1967**, 1913. (c) For other bent structures of unsaturated ylides, see: Bestmann, H. J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 349.

(30) (a) Jensen, P. *J. Mol. Spectrosc.* **1984**, *104*, 59. (b) Jensen, P.; Johns, J. W. C. *Ibid.* **1986**, *118*, 248. (c) Loses, R. L.; Sabin, J. R. *Ibid.* **1981**, *86*, 357. (d) Takeuchi, H.; Tasumi, M. *Ibid.* **1981**, *90*, 116.

(31) (a) Winnewisser, M.; Christiansen, J. J. *Chem. Phys. Lett.* **1976**, *37*, 270. (b) Winnewisser, M.; Peau, E. W.; Yamada, K.; Christiansen, J. J. *Z. Naturforsch., A* **1981**, *36*, 819. (c) Winnewisser, M.; Peau, E. W. *Chem. Phys.* **1982**, *71*, 377. (d) Winnewisser, M.; Peau, E. W. *Acta Phys. Hung.* **1984**, *55*, 33.



16

Because correlation effects are prominent in the evaluation of the potential well depth (in ref 6a, they stabilize the orthogonal bent form with respect to the planar form by 670 cm^{-1}), we think the former value of 433 cm^{-1} is a better estimate than the latter which does not take them into account.

The case of ethylenedione, O=C=C=O, is special in that the molecule is not bound with respect to two ground-state CO molecules.[32] Whereas the $^3\Sigma_g^-$ ground state is stable with respect to its dissociation products, CO($^3\Pi$) + CO($^1\Sigma^+$), the $^1\Delta_g$ state, which strictly correlates with two $^1\Sigma^+$ ground-state CO molecules, spontaneously distorts and relaxes, by trans-bending, toward its dissociation limit.[32a] Ethylenedithione, S=C=C=S, on the other hand, is bound in its $^3\Sigma_g^-$ ground state with respect to two ground-state CS molecules.[32b] Applying Carter and Goddard's rule to the C_2O_2 system confirms that the $^1\Sigma_g^+$ linear state, which correlates with 2 CO($^3\Pi$), is unbound by $\simeq$106 kcal/mol with respect to two ground-state CO molecules. This is in agreement with the CI estimate[32a] of 90 kcal/mol. Relation 2′ shows that a trans-bent "$^1\Delta_g$" state, built from two $^1\Sigma^+$ ground-state CO molecules, would be still higher in energy. For C_2S_2, Carter and Goddard's model predicts that the linear $^1\Sigma_g^+$ state should be bound by $\simeq$14 kcal/mol with respect to two ground-state CS molecules, while relation 2′ suggests that the "$^1\Delta_g$" potential surface would have a higher minimum.

B. Ketenes. The arguments used to account for the nonlinearity in cumulenones should suggest nonplanarity in some ketenes. In Table III, we applied condition 2″ to some typical ketenes and their thioketene analogues. Of course, the parent H_2C=C=O is expected to be planar, but, more surprising, F_2C=C=O also should not deviate from planarity despite its large $\Sigma\Delta E_{S\rightarrow T}$ of 189 kcal/mol, since f($E_{\sigma+\pi}$) is calculated to be just above at 192 kcal/mol.

We decided to perform ab initio calculations on difluoroketene, F_2C=C=O, in order to test our hypotheses and modelling. First, we undertook a comparative study of ketene, H_2C=C=O, and difluoroketene, F_2C=C=O, at a SCF-DZ level.[23] Both molecules were found to be planar. Their optimized geometries are given in Table IV. More significant differences are expected from the wagging force constants of the two molecules, since in difluoroketene f($E_{\sigma+\pi}$) is only ~3 kcal/mol larger than $\Sigma\Delta E_{S\rightarrow T}$. The normal coordinate force constants and harmonic vibrational frequencies, calculated at the SCF-DZ level of theory, are reported in Table V.[33] As expected, the force constant corresponding to the trans-wagging out-of-plane deformation of the skeleton dramatically decreases from H_2C=C=O to F_2C=C=O. The effect is strong enough to reverse the ordering cis-wagging < trans-wagging occurring in H_2C=C=O.

We next explored small deviations from planarity in F_2C=C=O at the SCF-DZd + CI level.[23,24] At the SCF-DZd level, the calculated geometry is still found planar, with the following parameters: CC = 1.306 Å, CO = 1.149 Å, CF = 1.317 Å, and FCF = 113.4°. When electron correlation is included, any F_2CC wagging is still not favored in energy, although the potential curve is very flat. Our CIPSI-CI procedure allows us to evaluate the correlation energy through diagonalization of a given set of determinants and application of a multireference Möller-Plesset second-order perturbation correction. Depending on the size of the subspace, correlation energy would favor small nonplanar distortions of the F_2C group but not enough to compensate the SCF energy loss (+0.5 kcal/mol for a wagging angle of 10°; +2.2 kcal/mol for a wagging angle of 20°).

Table IV. SCF-DZ Geometries for H_2C=C=O and F_2C=C=O[a]

	H_2CCO (C_{2v})	F_2CCO (C_{2v})
C=C	1.312 (1.314)	1.305
C=O	1.172 (1.161)	1.173
C—H (C—F)	1.080 (1.077)	1.360
HCH (FCF)	120.3 (122.2)	113.1

[a] In Å and degrees. Experimental values[15] in parentheses.

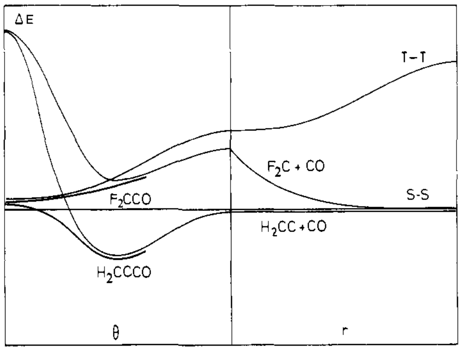
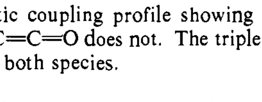


Figure 6. Schematic coupling profile showing why H_2C=C=C=O distorts whereas F_2C=C=O does not. The triplet-triplet curve, labeled T-T, is common to both species.

So F_2C=C=O definitely does not deviate from planarity, as our modelling predicts. On the other hand, it does predict that H_2C=C=C=O, which has about the same $\Sigma\Delta E_{S\rightarrow T}$, should distort and indeed it does. Figure 6 is a graphical explanation of the structural difference between F_2C=C=O and H_2C=C=C=O in spite of their similar $\Sigma\Delta E_{S\rightarrow T}$ (in this figure the triplet-triplet curve is common to both compounds). Note that F_2CCO is not bound with respect to singlet F_2C: + :CO, despite the large dissociation barrier. Actually at the SCF-DZd level F_2CCO is found to be 21 kcal/mol *above* the ground-state singlet F_2C + CO, this singlet dissociation being forbidden.[35]

Cyclopropylidenemethanone, **17**, is an example of a ketene



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which is known to have a nonplanar structure. Analysis of its microwave spectrum evidences a double well corresponding to two trans-bent structures.[36] The barrier separating the two minima is fairly small (38 cm^{-1}, i.e., 0.1 kcal/mol) but lies above the ground vibrational state. Applying condition 2″ actually predicts a nonplanar structure for cyclopropylidene methanone, as can be seen in Table III. Notice that we are closer to equality than inequality in condition 2″, suggesting a flat surface which is in agreement with experimental data.[36] Replacing the oxygen atom by a sulfur atom should definitely restore planarity. Replacing

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(32) (a) Haddon, R. C.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1975**, *97*, 1645. (b) Paine, G. P.; Schaefer, H. F., III; Haddon, R. C. *J. Am. Chem. Soc.* **1983**, *105*, 194. (c) For a recent attempt to trap C_2O_2, see, for instance: Birney, D. M.; Berson, J. A. *Tetrahedron* **1986**, *42*, 1561.

(33) For an accurate ab initio study of the electronic structure and the force field of H_2C=C=O, see: Allen, W. D.; Schaefer, H. F., III *J. Chem. Phys.* **1986**, *84*, 2212.

(34) The configuration interaction (CI) is performed with the CIPSI method: Daudey, J. P.; Malrieu, J. P. In *Current Aspects of Quantum Chemistry*; Carbo, T., Ed.; Elsevier: Amsterdam, 1982,; p 35.

(35) The SCF-DZd geometries for CF_2 and CO correspond to C-F = 1.284 Å, ∠FCF = 104.5°, C-O = 1.113 Å.

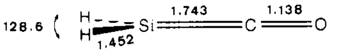
(36) (a) Brown, R. D.; Godfrey, P. D.; Kleibömer, B.; Champion, R.; Elmes, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 7715. (b) Brown, R. D.; Godfrey, P. D.; Kleibömer, B. *J. Mol. Spectrosc.* **1986**, *118*, 317.

Table V. SCF–DZ Normal Coordinate Force Constants and Vibrational Frequencies for $H_2C{=}C{=}O$ and $F_2C{=}C{=}O$

$H_2C{=}C{=}O$				$F_2C{=}C{=}O$			
symmetry	force constant (mdyn/Å)	freq (cm^{-1})	assignment	symmetry	force constant (mdyn/Å)	freq (cm^{-1}	assignment
b_1	0.5	486	CCO bend	b_1	0.5	215	CCO bend
b_2	1.2	561	cis-wag	b_2	0.5	263	trans-wag
b_2	2.6	843	trans-wag	b_2	1.2	386	cis-wag
b_1	4.0	1133	CH_2 rock	a_1	2.0	446	CF_2 sciss
a_1	17.0	1229	pseudosym CCO str	b_1	3.9	698	CF_2 rock
a_1	1.7	1547	CH_2 sciss	a_1	6.4	783	sym CF str
a_1	38.8	2250	pseudoantisym CCO str	b_1	14.1	1313	antisym CF str
a_1	5.9	3328	sym CH str	a_1	18.5	1523	pseudosym CCO str
b_1	16.6	3437	antisym CH str	a_1	42.5	2379	pseudoantisym CCO str

the cyclopropylidene fragment by a cyclopropenylidene fragment is also expected to restore planarity in spite of the large $\Delta E_{S\to T}$ for C_3H_2. Another suggestion which arises from Table III is that the wagging force constant for $H_2C{=}C{=}S$ should be significantly larger than that of $H_2C{=}C{=}O$, which happens to be experimentally verified.[37]

The second example we chose to illustrate by ab initio calculations is 1-silaketene, $H_2Si{=}C{=}O$. According to our modelling (see Table III), this molecule should be strongly bent. We have calculated the geometry of $H_2Si{=}C{=}O$ at the SCF-DZd level.[23] The planar C_{2v} structure, **18**, is found to be just a saddle point



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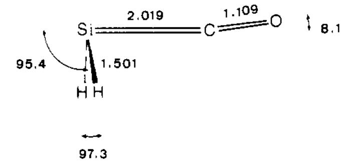

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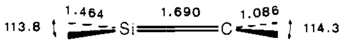
connecting the two forms of a trans-bent C_s structure, **19**. The planar C_{2v} transition state, **18**, lies 23 kcal/mol (at the SCF-DZd level) above the stable ground-state nonplanar absolute minimum **19**. This very bent structure deserves a few comments. The silylene–carbonyl composition is manifested not only by the bending of the SiH_2 group (note that it is bent with respect to Si–C or Si–C–O by more than 90°) but also by the intrinsic SiH_2 and CO geometries, together with the long Si–C distance. In fact, **18** is a π-bonded compound, but **19** is almost an intermolecular complex as illustrated by the very weak reaction energy $\Delta E = -10.2$ kcal/mol calculated at the SCF-DZd level for the reaction: $H_2Si\ (^1A_1) + CO\ (^1\Sigma^+) \rightarrow H_2SiCO\ (^1A')$. The silene-like nature of **18** and silylene + carbonyl-like nature of **19** is made even more conspicuous when comparing their geometrical parameters with those of $H_2Si{=}CH_2$, **20**, and of $H_2Si(^1A_1)$ and CO, **21** calculated in the same conditions. It is clear that $H_2Si{=}C{=}O$ is more like a silylene–carbonyl complex, in which both fragments keep their identity, than like a 1-silaketene molecule. Two factors may account for its "overbent" structure ($\theta > 90°$): first, the vacant p_π orbital of the carbonyl which receives the n_σ pair on silicon is partly occupied, as already mentioned; second, and more influential, the π-type occupied SiH bonding MO of SiH_2 interacts with the empty π^* antibonding MO of CO, **22**, possibly inducing the overbending.



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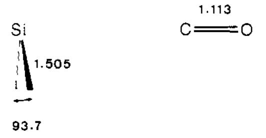

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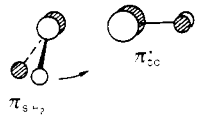

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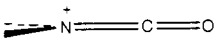
There is little doubt that a similar strongly trans-bent structure occurs in 1-germaketene or 1-stannaketene. Note that the distorted structure of 1-silaketene was obtained at the SCF level, unlike that of propadienone. Notice also that replacing the oxygen atom in $H_2Si{=}C{=}O$ by a sulfur atom should not restore planarity although here we are close to equality in (2″), suggesting a weaker bending angle and a flatter surface. Table III also indicates that 2-silaketene and 2-silathioketene are expected to be planar whereas their difluoro derivatives are not. However, $H_2C{=}Si{=}O$ and $F_2C{=}Si{=}S$ should have flat surfaces.

The previous analysis is valid if we replace the carbene part of the ketene by any valence-isoelectronic fragment such as NR_2^+ or PR_2^+. NH_2^+ and PH_2^+ happen to have very different $\Delta E_{S\to T}$ (−30 and +16 kcal/mol, respectively),[8] so we now understand (see Table III) why H_2NCO^+ has a planar structure, **23**,[38] while H_2PCO^+ has a trans-bent distorted structure, **24**.[39]



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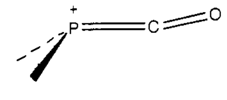

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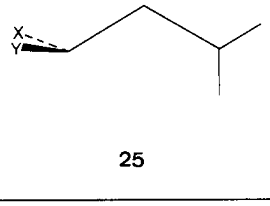
We wish to point out, lastly, that some substituted ketenes could be intrinsically chiral and that most unsymmetrically substituted 1-sila-, -germa-, or -stannaketenes should be chiral since the inversion barrier separating the two trans-bent enantiomers is quite sizable as we saw for $H_2Si{=}C{=}O$.

C. Allenes. An allene can be considered as a carbene + a vinylidene. From the previously developed arguments, it may be suggested that for a given carbene moiety of large $\Delta E_{S\to T}$, deviations from linearity might occur, **25**, or at least enhanced



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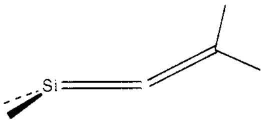
[37] Kroto, H. W.; McNaughton, D. *J. Mol. Spectrosc.* **1985**, *114*, 473. The mass effect should lower the vibrational frequencies from H_2CCO to H_2CCS. The frequency corresponding to the wagging mode is actually the only one which is increased instead of being lowered.

[38] Ha, T. K.; Nguyen, M. T. *J. Mol. Struct.* (*THEOCHEM.*) **1982**, *88*, 335.

[39] Nguyen, M. T.; Hegarty, A. F.; McGinn, M. A.; Ruelle, P. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1991.

fluxionality might be observed. In Table I, the proposed modelling rules are applied to some allenic and silaallenic systems. Neither the parent allene, $H_2C{=}C{=}CH_2$, nor 1,1-difluoroallene, $F_2C{=}C{=}CH_2$, are expected to deviate from linearity, which happens to be experimentally verified.[15] However, $F_2C{=}C{=}CH_2$ is not far from equality, which suggests (i) a low wagging frequency for this compound and (ii) a possible distortion in further substituted 1,1-difluoroallenes.

Condition 2 is satisfied in 1-silaallene which should therefore deviate from linearity. This molecule was optimized at the SCF level by two groups.[40] In both works a linear C_{2v} geometry is reported. We suspect that in both cases the symmetry has been fixed as is usually done when operating with a gradient technique. If it is the case, we suggest that a check should be made at SCF and CI levels, whether the C_{2v} linear arrangement is a real minimum or only a saddle point between two trans-bent forms **26**. Of course, stronger distortions are expected when replacing SiH_2 by SiF_2, GeH_2, SnH_2, or GeF_2. On the other hand, 2-silaallene is not expected to deviate from a linear D_{2d} structure. This was predicted by ab initio SCF calculations.[41] 1,1-Difluoro-2-silaallene should distort, however. Cyclopropenylideneallene is on the borderline, but π-conjugation (π-Hückel arguments lead to a π-delocalization of 3β for methylenecyclopropane) should in this case enhance $E_{\sigma+\pi}$ and favor planarity.



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D. Cumulenes. The first real parent cumulene is butatriene, $H_2C{=}C{=}C{=}CH_2$, formally made by coupling two vinylidene fragments. Since $\Sigma\Delta E_{S\to T}$ = 92 kcal/mol, condition 2 is satisfied (92 > 86) and a planar bent C_{2h} distortion could ensue. However, because of the neglect of the π net charge brought by hyperconjugation in vinylidene, we think this system is on the borderline, and it cannot be settled whether the barrier to linearity is *above* the ground vibrational state or not. Only a weak force constant for a trans in-plane deformation can be predicted. In longer cumulenes, one or both fragments are longer unsaturated carbenes. These have singlet ground states but have a smaller $\Delta E_{S\to T}$ than vinylidene. For instance, $H_2C{=}C{=}C$: has a $\Delta E_{S\to T}$ calculated at 33 kcal/mol,[16b] which implies that condition 2 is no longer satisfied in pentatetraene, $H_2C{=}C{=}C{=}C{=}CH_2$, since $\Sigma\Delta E_{S\to T}$ is only 79 kcal/mol. Moreover, with longer unsaturated carbenes, a significant π net charge should be taken into account which definitely discards deformations.

E. Alkynes. Unlike its parent acetylene, **27a**, silaacetylene (or silaethyne) exhibits a peculiar behavior when its geometry is optimized by quantum calculations.[42,43] At the SCF level, no minimum is found for any linear or trans-bent structure corresponding to HSi≡CH. If electron correlation is included, a real minimum occurs for a trans-bent structure, **27b**.[42,43] We can risk a rationale based on the multiplet ordering of the fragments CH and SiH in the spirit of what has been developed previously. A typical acetylenic system can be seen as two interacting methyne fragments in a quartet configuration corresponding to $n_\sigma p_{\pi x} p_{\pi y}$ single occupation, as shown in **28a** (for clarity, we omit the p_π orbitals which are perpendicular to the plane and whose occupancy will not change along the considered distortion). This configuration is associated with the $^4\Sigma^-$ state, which is the first excited state for both CH and SiH. Both diatomic molecules have a $^2\Pi_r$ ground state corresponding to a $n_\sigma^2 p_{\pi x}$ configuration. The coupling of two such configurations would favor a trans-bent structure **28b**. In CH the $^2\Pi_r \to {}^4\Sigma^-$ separation is only 17 kcal/mol.[25] Twice this promotion energy is largely compensated by the formation of a strong C≡C triple bond in acetylene ($E_{C\equiv C} \sim$ 200 kcal/mol) so that **28a** is definitely favored over **28b** and H—C≡C—H is linear. The $^2\Pi_r \to {}^4\Sigma^-$ separation happens to be larger in SiH (37 kcal/mol)[44] so that the contribution of **28b** to the bonding in H—Si≡C—H is now more significant and partly induces its trans-bending, all the more that $E_{Si\equiv C}$ is much weaker than $E_{C\equiv C}$. In disilaacetylene or disilyne, HSi≡SiH, the trans-bent structure is also found to be a real minimum when correlation is included,[45] while the linear form is found to be only a saddle point at both SCF and electron correlation levels.[45-48] Note, however, that the absolute minimum on the Si_2H_2 potential surface occurs for a nonplanar bridged structure. Similar results are expected for singlet FC≡SiF although a twisted geometry (i.e., non-trans-bent, nonplanar, and nonlinear geometry) has been reported, but this geometry was calculated only at the SCF level with a 3-21G (i.e., DZ) basis set.[49] The genuine π bond in the acetylenic system kept aside, the use of simple conditions 1 and 2 lead to satisfactory results:

a b

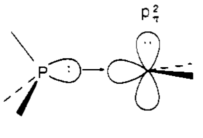
27

a b

28

	$^1/_2E_{\sigma+1\pi}$	$\Sigma\Delta E(^2\Pi_r{\to}^4\Sigma^-)$	expected structure
HC≡CH	86	34	linear
HSi≡CH	52–56	54	borderline
HSi≡SiH	37	74	nonlinear

F. Ylides and Diazo Compounds. Bonding in phosphonium ylides can be schematized as the interaction of a phosphine with a p_π^2 closed-shell singlet excited carbene, **29**. The energy required for reaching the p_π^2 configuration from a n_σ^2 or $n_\sigma p_\pi$ configuration is largely compensated by the building of a ylilic bond which is basically a dative bond (phosphine lone pair → carbene empty n_σ) plus a partial back donation (carbene occupied p_π → phosphine empty d_π). As in the previous discussion on olefins, there is a



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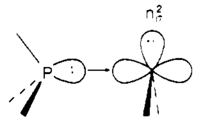

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Table VI. Relation between the Singlet-Triplet Separation of Some CR_2 Carbenes and the Extent of the PCR_2 Pyramidalization in the Phosphonium Ylide $H_3P{=}CR_2$, according to the SCF-Calculated Structures of Ref 52

	$\Delta E_{S\to T}$, kcal/mol	$\sum\alpha$, deg
$C(CF_3)_2$	-15^a	360
CH_2	-10^b	354
CHF	$+13^c$	338
CF_2	$+50^b$	313

^{a}Estimated from ref 53a. ^{b}Reference 8. Reference 53b.

balance between the energy required for making an excited configuration (here p_π^2) and the energy gained by making a new bond (here the ylilic bond). One understands easily that when the $n_\sigma \to p_\pi$ separation in the carbene-like species is too large in regard to the energy of the ylilic bond which is created, a bent arrangement preserving the n_σ^2 configuration will be preferred, **30**. The $n_\sigma^2 \to p_\pi^2$ promotion energy would strictly relate to the $1^1A_1 \to 2^1A_1$ singlet–singlet separation in the methylene-like species. In fact, this separation is proportional to the simple n_σ–p_π gap which is reflected by the simple singlet–triplet separation $\Delta E_{S\to T}$ (the $1^1A_1 \to 2^1A_1$ separation is reasonably approximated by $2|\Delta E_{S\to T}|$). Methylenephosphorane and many alkyl-substituted methylenephosphoranes have a planar or quasi-planar PCR_2 arrangement with a very flat potential surface with respect to pyramidaliation of the CR_2 group. This is related to the triplet ground state of CH_2 or to the low $\Delta E_{S\to T}$ of alkyl-substituted carbenes. We have pointed out elsewhere[50] that the strongly bent structure of Ph_3PGeCl_2, actually named as a phosphine–germylene complex,[51] can be related to the singlet ground state (with a high $\Delta E_{S\to T}$) of the germylene part.

Another neat illustration of the propensity to a bent geometry (induced by a predominant contribution of **30**), with increasing $\Delta E_{S\to T}$ of the CR_2 fragment, emerges from the SCF-calculated structures of $H_3P{=}CH_2$, $H_3P{=}CHF$, $H_3P{=}CF_2$, and $H_3P{=}C(CF_3)_2$.[52] Table VI displays the sums of the valence angles around the carbon atom as calculated by Dixon and Smart for this series of compounds.[52] This sum represents the extent of pyramidazliation at this atom ($\Sigma\alpha = 360°$ means a planar arrangement; $\Sigma\alpha = 270°$ would mean a cubic pyramidalized arrangement). The dependence of the bending on $\Delta E_{S\to T}$ is quite manifest and incidentally happens to be quasi-linear ($r^2 = 0.997$). H_3PCF_2 has an even more peculiar structure: at the SCF level, not only the FCF plane is very bent but also the whole structure corresponds to a nearly intermolecular complex with a very long P–C bond and a very weak energy for its dissociation into PH_3 + $CF_2(^1A_1)$.

The bonding in diazo compounds CR_2N_2 is similar to the bonding in phosphonium ylides. Here, the N–C bond is mainly a dative bond from a sp lone pair of N_2 toward the n_σ empty orbital of the carbene part, $N{\equiv}N|{\to}\bar{C}R_2$, as in **29**. The $d_\pi \leftarrow p_\pi$ back-bonding of the ylide is now a $\pi^*_{N_2} \leftarrow p_\pi$ back-bonding, which is embodied in the formal chemist's notation $N{=}N{=}CR_2$. If the carbene part has a low $n_\sigma \to p_\pi$ separation, reflected by a low $\Delta E_{S\to T}$, linear N–N–C and planar N–CR_2 arrangements will prevail as in **29** (replacing the PR_3 moiety by N_2). Diazomethane, CH_2N_2, which has a planar C_{2v} geometry, belongs to this category.[54a] If the carbene part has a large $n_\sigma \to p_\pi$ separation, reflected by a large $\Delta E_{S\to T}$, the molecule will tend to distort in a trans-bent way, with angular N–N–C and nonplanar N–CR_2 arrangements, in order to maximize the $sp_{N_2} \to p_\pi$ and $\pi^*_{N_2} \leftarrow n_\sigma$ interactions. Diazoethenes, the carbene part of which are vinylidenes, $R_2C{=}C$, bearing large $\Delta E_{S\to T}$, actually exhibit such trans-bent geometries.[54b] One can therefore expect that several diazo compounds should be bent. Such is the case of CF_2N_2, which should display the same type of bending as CF_2PH_3.[54c]

Extension to Organotransition Metal Chemistry

The isolobal analogy,[55] which provides a structural isomorphism between organic and organometallic fragments, has proven to be fruitful in understanding the bonding in some peculiar transition metal complexes. Let us use it and see whether nonclassical distortions might occur when transition metal atoms are involved in a molecular system. Methylene, CH_2, is isolobal with a d^8 C_{2v} ML_4 metallic fragment which in turn is isolobal with a d^{10} C_{2v} ML_2 fragment:

$$CH_2 \underset{\smile}{\longleftrightarrow} d^8\ C_{2v}\ ML_4 \underset{\smile}{\longleftrightarrow} d^{10}\ C_{2v}\ ML_2$$

In ML_4, the orbitals which compare with the n_σ and p_π carbene orbitals are two hybrids, a_1 and b_2, located on the metal atom, with a_1 being *above* b_2. When both hybrids are singly occupied, the coupling of two such fragments leads to a dinuclear compound $L_4M{=}ML_4$ involving a formally double metal–metal bond **31**.[55]

31

Should the b_2–a_1 separation be very large, a b_2^2 configuration would be preferred at each fragment, and it might be more advantageous to make two dative bonds $b_2 \to a_1$ and tilt each ML_4 part away in a $D_{2h} \to C_{2h}$ distorsion, **32**, quite analogously to the previously described olefin distorsions. Note that the optimal tilting (or rocking) angle should be around 25° instead of 45° for the olefin distortions. We have explored such possibilities by performing extended Hückel[56] calculations on a model complex, the fragments of which have a typically large b_2–a_1 gap. We chose a d^{10} C_{2v} ML_2 fragment, $Ni(PH_3)_2$, since the arguments developed for d^8 ML_4 are strictly valid for d^{10} ML_2. $Ni(PH_3)_2$ has a b_2–a_1 gap of about 6 eV, whereas a typical d^8 C_{2v} ML_4 fragment such as $Fe(CO)_4$ has a b_2–a_1 gap of only 1–2 eV. In the dinuclear complex $(PH_3)_2Ni{=}Ni(PH_3)_2$ we therefore expect a planar $D_{2h} \to C_{2h}$ distortion to occur, **33**. The EHT calculations[57] actually disclose

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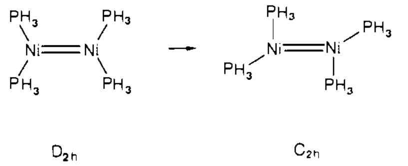

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(52) Dixon, D. A.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 7172.

(53) (a) Dixon, D. A. *J. Phys. Chem.* **1986**, *90*, 54. (b) Scuseria, G. E.; Durān, M.; Maclagan, R. G. A. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1986**, *108*, 3248.

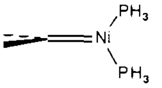
(54) (a) Cox, A. P.; Thomas, L. F.; Sheridan, J. *Nature* (*London*) **1958**, *181*, 1000. (b) Lahti, P. M. *Chem. Phys. Lett.* **1986**, *133*, 139. (c) For a comparative theoretical study of the geometry of various diazo molecules, see: Moffat, J. B. *J. Phys. Chem.* **1978**, *82*, 1083. In this work, however, no bent distortion was allowed. In contrast with most theoretical studies on diazo compounds, Bastide and Henri-Rousseau have explored a nonplanar deformation on diazomethane (Bastide, J.; Henri-Rousseau, O. *Tetrahedron Lett.* **1972**, *29*, 2979). Interestingly enough, the CNDO/2 method gives a local minimum for a simple C–N–N folding of 25°.

(55) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

(56) Hoffmann, R. *J. Chem. Phys.* **1967**, *39*, 1397.

this trend for various NiNi distances although the corresponding potential curves (given in Figure 7) involve weak stabilization energies.

Can such a distortion occur at a formally double metal–carbene bond? The answer is yes, providing that the carbene has its b_2 orbital *below* a_1, which means that both the metallic fragment and the carbene part have a b_2, a_1 ordering. Simple methylene for instance, does not satisfy this criterium since it has a typical a_1, b_2 ordering. So, the model complex $H_2C{=}Ni(PH_3)_2$ should not distort from **34** to **35** in which H_2CNi distorts out of plane and $CNi(PH_3)_2$ distorts in plane. EHT calculations[57] actually lead to an energy increase for such deformations (e.g., $\Delta E = +2$ kcal/mol for $\theta = 10°$). Cyclopentadienylidene, on the other hand, does display a b_2, a_1 ordering. The p_π b_2-type carbene orbital is here lowered because of its involvement in the six-electron five-membered aromatic π system, **36**. In the model complex $H_4C_5{=}Ni(PH_3)_2$, we therefore expect the distortion **37** to occur since both fragments bear an orbital pattern (occupied b_2, empty a_1) with a large b_2–a_1 gap on one side. EHT calculations[57] clearly confirm this structural trend as can be seen in Figure 8.



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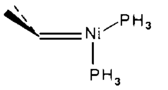

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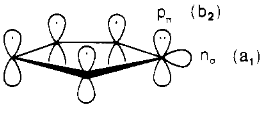

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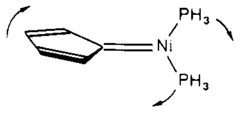

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The modelling developed in main group chemistry seems therefore to hold qualitatively in transition-metal chemistry. This should be kept in mind when explaining and rationalizing peculiar structures encountered in this very rich field of chemistry.

Concluding Remarks

Carter and Goddard have evidenced the involvement of the triplet state of carbenes in the building of olefins, showing how the strength of a $\sigma + \pi$ double bond is basically governed by the singlet–triplet separation of its carbene fragments.[9] This work suggests a further implication: when singlet configurations are preferred by far, they work to distort the geometry in order to maximize their own interaction, each carbene thus keeping its ground-state closed-shell configuration. In other words, fragments tend to preserve their individualities, when possible.

Note that all trans-bent distortions accounted for in the present work (except in the ylide section) are *non*-Gillespie in nature. They may lead to stable distorted isomers, observable at room temperature. They may also not be observed if the ground vibrational state is sufficiently delocalized over the barrier between the equivalent trans-deformed isomers. Last, they may simply result in a weakening of wagging force constants.

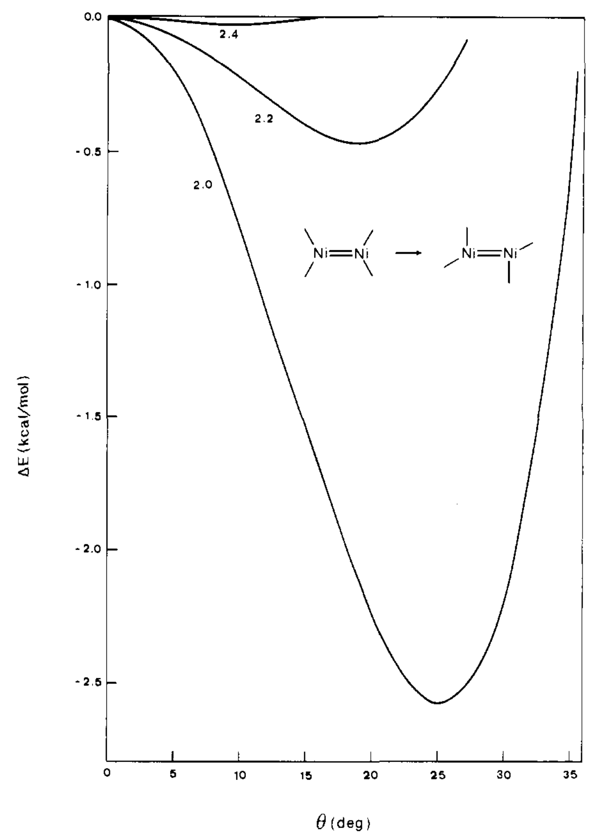

Figure 7. EHT energy variation for the $D_{2h} \rightarrow C_{2h}$ planar distortion in $(PH_3)_2Ni{=}Ni(PH_3)_2$. Three NiNi distances are considered: 2.0, 2.2, and 2.4 Å.

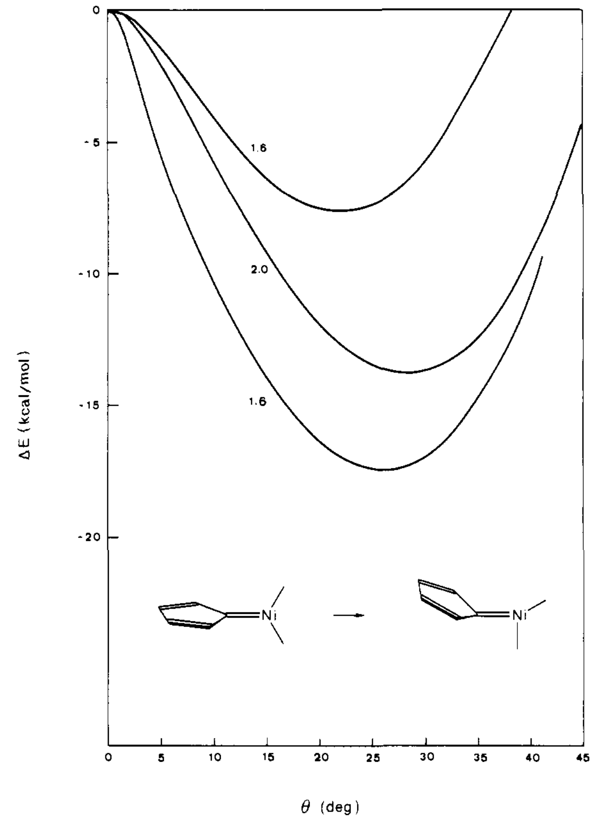

Figure 8. EHT energy variation for the $C_{2v} \rightarrow C_s$ distortion in $H_4C_5{=}Ni(PH_3)_2$. Three CNi distances are considered: 1.6, 1.8, and 2.0 Å.

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[57] The following EHT parameters were used. Ni: H_{ii} (eV) = −9.13, −5.12, and −13.44 for 4s, 4p, and 3d respectively; $\zeta = 2.1$ (4s and 4p), 5.75, and 2.0 (3d, double-ζ: $C_1 = 0.59995$, $C_2 = 0.59821$). P: $H_{ii}(3s) = -18.6$, $H_{ii}(3p) = -14.00$; $\zeta(3s,3p) = 1.6$. C: $H_{ii}(2s) = -21.4$, $H_{ii}(2p) = -11.4$, $\zeta(2s,2p) = 1.625$. H: $H_{ii} = -13.6$, $\zeta = 1.3$. The following geometrical parameters were used: Ni–P = 2.15 Å, P–H = 1.42 Å, PNiP = 120°, HPH = 93°. C_5H_4 is assumed to have a pseudo-D_{5h} symmetry, with C–C = 1.42 Å and C–H = 1.08 Å. For $H_2CNi(PH_3)_2$, C–H = 1.08 Å, HCH = 120°, and C–Ni = 2.0 Å.

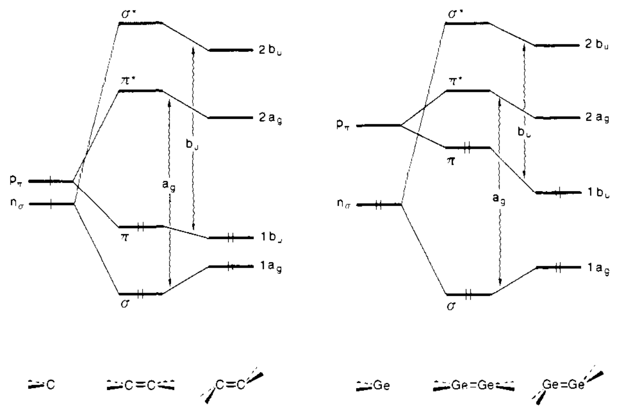


Figure 9. Simplified MO diagram relating a carbene, a planar olefin, and a trans-bent olefin: left, ethylene (C_2H_4); right, digermene (Ge_2H_4).

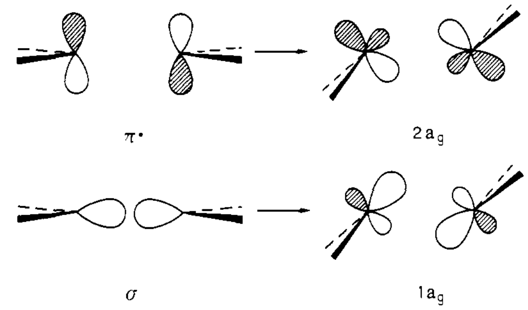
The proposed model remains quite crude, but it has the advantage of directly evidencing the leading role of mere singlet–triplet separations.[58] It accounts for the crucial importance of electronic correlation when predicting certain structures and wagging frequencies.[59] More accurate and numerous values of the $\Delta E_{S\to T}$ separations would be welcome for further suggestions and checking of the model.

The influence of singlet inclination of fragments on fluxionality has been theoretically and experimentally confirmed in main group chemistry. The present paper also suggests some tentative extensions to transition metal chemistry. The versatility of multiple bonds between classical open-shell alignments and trans-bent singlet–singlet interactions is a general feature which may have consequences in structures, spectroscopy, chirality, and reactivity over a large domain of chemistry.

Appendix I. One-Electron MO Treatment of the Trans-Bent Distortion in C_2H_4 and Ge_2H_4

Pure one-electron arguments can account for the trans-bent structure of digermene, $H_2Ge{=}GeH_2$. From simple EHT calculations,[60] digermene is found to be trans-bent with a wagging angle θ of 40° and an inversion barrier ΔE of 4 kcal/mol. The same method gives a planar ethylene undergoing a destabilization energy of +19 kcal/mol when distorted at a similar wagging angle ($\theta = 40°$). The fairly accurate result of EHT on digermene indicates that the cause of the bending can be sought in one-electron MO arguments. Using Walsh diagrams and FMO analysis of the wave functions, we attempted to determine the events occurring when ethylene and digermene are distorted from a planar geometry to a typically trans-bent geometry ($\theta = 40°$).[61]

As soon as the olefin begins to bend, the σ and π^* MOs mix in since they are both of a_g symmetry, **38**. σ is pushed up in energy while π^* is pushed down. In fact, the mixing attenuates these energy changes. A similar mixing occurs for π and σ^* which are both of b_u symmetry, **39**. Without mixing, π should go up and σ^* should go down. Because of the mixing, however, $1b_u$ is pushed down in energy and $2b_u$ is also pushed down, its fall in energy also being attenuated here. Since the total energy rises with bending for C_2H_4 while it drops with bending for Ge_2H_4, this means that occupied $1a_g$ rises more quickly than occupied $1b_u$ falls in C_2H_4 while occupied $1b_u$ falls more quickly than $1a_g$ rises in Ge_2H_4. Examination of energy levels and wave functions shows that the a_g mixing and $1a_g$ and $2a_g$ energy changes occur to the same extent in both olefins. The difference lies in the b_u mixing which is significantly stronger in digermene than in ethylene. Consequently the $1b_u$ stabilization is larger in digermene (−0.47 eV) than in ethylene (−0.19 eV) while the $1a_g$ destabilization is close in both compounds (+0.32 and +0.38 V, respectively). In Figure 9 we have tried to schematize why b_u mixing is more pronounced in Ge_2H_4 than in C_2H_4. The π–σ^* separation is much smaller in degermene than in ethylene owing to (i) the larger n_σ–p_π separation in germylene GeH_2 (related to its larger $\Delta E_{S\to T}$) and (ii) the weaker π-bonding in digermene. Note that these two effects work in opposite directions for the σ–π^* separation, which becomes similar in both ethylene and digermene, inducing the comparable a_g mixing.



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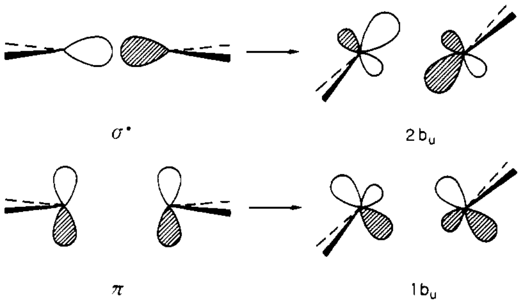

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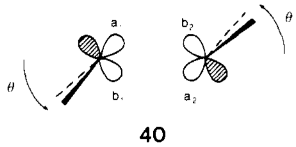
Appendix II. Valence Bond Energy for a Dative Bent Double Bond

a. Wave Functions. The valence bond limiting wave function for two interacting *triplet* carbenes may be expressed, according to **40**, as At short distances where $\lambda \simeq \mu$, ψ_T can be written as



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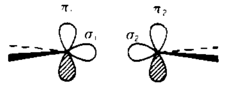

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$$\psi_T = \lambda\{|a_1b_1\bar{a}_2\bar{b}_2| + |\bar{a}_1\bar{b}_1a_2b_2|\} + \mu\{|a_1\bar{b}_1a_2\bar{b}_2| + |\bar{a}_1b_1\bar{a}_2b_2|\}$$

the antisymmetrized product of the neutral singlet functions:

$$\psi_T = \tfrac{1}{2}\mathcal{A}\{(a_1\bar{a}_2 + a_2\bar{a}_1)(b_1\bar{b}_2 + b_2\bar{b}_1)\}$$

which, for a planar arrangement, **41**, becomes

$$\psi_T = \tfrac{1}{2}\mathcal{A}\{(\sigma_1\bar{\sigma}_2 + \sigma_2\bar{\sigma}_1)(\pi_1\bar{\pi}_2 + \pi_2\bar{\pi}_1)\} \qquad (3)$$

The limiting valence bond wave function for two interacting *singlet* carbenes is

$$\psi_S = |a_1\bar{a}_1a_2\bar{a}_2| \qquad (4)$$

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(58) For another structural implication of singlet–triplet separations in delocalized systems, see: Shaik, S.; Bar, R. *Nouv. J. Chim.* **1984**, *8*, 411. Shaik, S.; Hiberty, Ph.; Ohanessian, G.; Lefour, J. M. *Ibid.* **1985**, *9*, 385.

(59) The sensitivity of wagging force constants to electronic correlation is further illustrated by a recent work on $H_2Si{=}CH_2$ (Colvin, M. E.; Kobayashi, J.; Bicerano, J.; Schaefer, H. F., III *J. Chem. Phys.* **1986**, *85*, 4563): the CI lowers all vibrational frequencies by 1–5% except for the two wagging modes which are lowered by 11 and 22%.

(60) The following EHT parameters were used. Ge: $H_{ii}(4s) = -18.57$ eV, $H_{ii}(4p) = -9.43$ eV; $\zeta(4s) = 2.01$, $\zeta(4p) = 1.70$. C: $H_{ii}(2s) = -21.40$ eV, $H_{ii}(2p) = -11.40$ eV; $\zeta(2s) = \zeta(2p) = 1.625$. H: see footnote 57. The following geometrical parameters were used: CC = 1.34 Å, CH = 1.09 Å, HCH = 120°, GeGe = 2.30 Å, GeH = 1.53 Å, and HGeH = 111°.

(61) The MO arguments on σ–π mixing used in Appendix I can be found also in ref 2f and 2g and in: (a) Volland, W. V.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 533. (b) Strozier, R. W.; Caramella, P.; Houk, K. N. *Ibid.* **1979**, *101*, 1340.

(62) **Note Added in Proof**: Recently, $H_2C{=}C{=}C{=}S$ was found to be linear: Brown, R. D.; Godfrey, P. D.; Elmes, P. S.; McNaughton, D. *J. Chem. Soc., Chem. Commun.* **1987**, 573.

b. Energies. The bonding energy originates from the mixing with ionic structures lying at an energy U above the neutral ones. For the typical planar $\sigma + \pi$ double bond, this delocalization energy can be expressed straight from (3) at the second-order of perturbation:

$$\epsilon_T = (4/U)\{F^2_{\sigma_1\sigma_2} + F^2_{\pi_1\pi_2}\} = E_\sigma + E_\pi = E_{\sigma+\pi} \qquad (5)$$

where F_{xy}, standing for $\langle x|F|y\rangle$, is the classical hopping integral. Similarly, the second-order energy associated with (4) originates from the $a_1 \rightarrow b_2$ and $a_2 \rightarrow b_1$ delocalizations:

$$\epsilon_S = (4/U)F^2_{a_1b_2} \qquad (6)$$

Assuming that all axial overlaps are equal and all lateral overlaps are equal, one may express **40** in terms of **41** in the simplified way:

$$a_1 = \cos\theta\ \sigma_1 + \sin\theta\ \pi_1 \qquad (7)$$

$$a_2 = \cos\theta\ \sigma_2 - \sin\theta\ \pi_2 \qquad (8)$$

$$b_1 = \sin\theta\ \sigma_1 - \cos\theta\ \pi_1 \qquad (9)$$

$$b_2 = \sin\theta\ \sigma_2 + \cos\theta\ \pi_2 \qquad (10)$$

Hence $F_{a_1b_2}$ can be written

$$F_{a_1b_2} = \langle a_1|F|b_2\rangle = \cos\theta\sin\theta\ (F_{\sigma_1\sigma_2} + F_{\pi_1\pi_2})$$

For $\theta = 45°$

$$F_{a_1b_2} = \tfrac{1}{2}(F_{\sigma_1\sigma_2} + F_{\pi_1\pi_2})$$

and (6) becomes

$$\epsilon_S = (1/U)(F_{\sigma_1\sigma_2} + F_{\pi_1\pi_2})^2$$

which, combined with (5), leads to

$$\epsilon_S = \tfrac{1}{4}(E_\sigma + E_\pi + 2\sqrt{E_\sigma E_\pi})$$

If $E_\pi \simeq E_\sigma$, the depth of the singlet–singlet potential well is therefore, at 45°:

$$\epsilon_S \simeq E_\sigma \simeq \tfrac{1}{2}(E_\sigma + E_\pi) = \tfrac{1}{2}E_{\sigma+\pi}$$

Note that the interaction between ψ_T and ψ_S

$$\langle\psi_T|H|\psi_S\rangle = (a_1b_2,b_1a_2)$$

is a bielectronic bicentric integral involving four AOs and should remain small. This legitimates considering only the energies of ψ_T and ψ_S before their interaction, in the qualitative discussion about the potential surfaces.

c. Refinement for π-Conjugated Carbenes. When the substituents X of a carbene CX_2 have π lone pairs, the p_π AO of the central atom is partly occupied in the singlet state. The occupied symmetrical π orbital may be written

$$\pi = \mu p_c + \nu(1/\sqrt{2})(p_{X1} + p_{X2})$$

where $\mu^2 = q$ is the π net charge on the central carbon atom in the singlet state. The virtual π^* MO of the carbene is therefore partly delocalized:

$$\pi^* = \nu p_c - \mu(1/\sqrt{2})(p_{X1} + p_{X2})$$

This π-delocalization results in two effects.

(i) First, a π-repulsion appears when two carbenes are brought together in trans-orthogonal approach **6** (step 1). This repulsion is proportional to the square of the overlap between the two occupied π MOs. Because of the trans arrangement, this overlap is only a function of the overlap between the two p_π carbon AOs:

$$\langle\pi_1|\pi_2\rangle = \mu_1\mu_2\langle p_{c_1}|p_{c_2}\rangle$$

The repulsion energy is therefore proportional to the product of the π net charges at each carbon atom:

$$\mathcal{R} = k\langle\pi_1|\pi_2\rangle^2 = \alpha q_1 q_2$$

The proportionality factor can be evaluated by calculating the repulsion between two lone pairs (4α) or two electrons of parallel spins (α).

(ii) Second, the delocalization energy is reduced in the trans-bent form since

$$F_{a_1\pi_2^*} = \nu_2 F_{a_1b_2} \qquad (11)$$

and

$$F_{a_2\pi_1^*} = \nu_1 F_{a_2b_1} \qquad (12)$$

The delocalization energy for the singlet–singlet surface is now

$$\epsilon_s = (2/U)(F^2_{a_1\pi_2^*} + F^2_{a_2\pi_1^*})$$

Since $\nu^2 = 1 - q$, ϵ_s is written

$$\epsilon_s = (2/U)\{F^2_{a_1b_2}(1 - q_2) + F^2_{a_2b_1}(1 - q_1)\} \qquad (13)$$

For symmetry reasons:

$$\epsilon_s = \frac{4}{U}F^2_{a_1b_2}\left(1 - \frac{q_1 + q_2}{2}\right)$$

As developed previously for $\theta = 45°$, the depth of the singlet–singlet potential well is finally

$$\epsilon_s \simeq \frac{1}{2}E_{\sigma+\pi}\left(1 - \frac{q_1 + q_2}{2}\right)$$

d. Case Where CO Is Involved. When CO is involved as a fragment, because of a larger isotropy at its carbene end, the C–C–O frame remains practically linear; i.e., θ_2, the right-hand side θ in **40**, is zero or negligible at the equilibrium geometry, as appears from all experimental information. Equations 11 to 13 remain valid but eq 8 and 10 are now simplified since $\theta_2 = 0$ (see **10**). a_2 and b_2 can be written straight, as in **41**, $a_2 = \sigma_2$ and $b_2 = \pi_2$. Consequently, for $\theta_1 = 45°$:

$$F_{a_1b_2} = (1/\sqrt{2})F_{\pi_1\pi_2}$$

and

$$F_{a_2b_1} = (1/\sqrt{2})F_{\sigma_1\sigma_2}$$

and (13) becomes

$$\epsilon_s = (1/U)\{F^2_{\pi_1\pi_2}2(1 - q_2) + F^2_{\sigma_1\sigma_2}(1 - q_1)\}$$

$$\epsilon_s = \tfrac{1}{4}\{E_\pi(1 - q_2) + E_\sigma(1 - q_1)\}$$

$$\epsilon_s \simeq E_{\sigma+\pi}\left(\frac{1}{4} - \frac{q_1 + q_2}{8}\right)$$