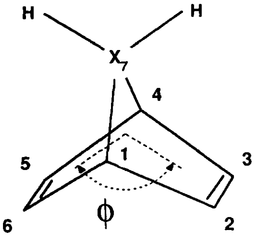
An *ab initio* SCF MO Study of the Electronic Structure of 7-Germanorbornadiene and 7-Stannanorbornadiene: Two Molecules Predicted to have an Inverted Sequence of π Levels

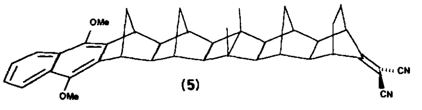
Michael N. Paddon-Row* and Stephen S. Wong
Department of Organic Chemistry, University of New South Wales, PO Box 1, Kensington, NSW 2033, Australia
Kenneth D. Jordan*
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, USA

The geometries of 7-germanorbornadiene (**3**) and 7-stannanorbornadiene (**4**) have been optimized, under C_{2v} symmetry constraint, using the HF/STO-3G and the HF/STO-3G* levels of theory. It is found that both (**3**) and (**4**) possess an inverted sequence of π levels, that is, the π_- (b_1) orbital lies energetically below the $\pi_+(a_1)$ orbital. This finding is consistent with the recently calculated inverted sequence of π levels found for 7-silanorbornadiene (**2**) but is in contrast to that found for the parent hydrocarbon diene, norbornadiene (**1**) in which the normal sequence of π orbitals (that is, π_+ lies below π_-) obtains. The degree of level inversion, as measured by the energy difference between the π_+ and the π_- canonical MO (CMO) levels, increases along the series: (**2**) (−0.17 eV) < (**3**) (−0.26 eV) < (**4**) (−0.87 eV) (STO-3G). It is proposed that the major causative factor of this trend is the increase in the strength of through-bond (TB) interactions between the π_- orbital and the C1–X7–C4 sigma MOs, as X changes from Si to Ge to Sn. In contrast with the π manifold, the sequence of π* levels in (**1**)–(**4**) is normal; indeed, the STO-3G energy difference between the π^*_- and π^*_+ CMO levels increases along the series: (**1**) (1.76 eV) ≈ (**2**) (1.70 eV) < (**3**) (2.02 eV) < (**4**) (2.67 eV), the value for (**4**) being remarkably large. This trend is explained in terms of TS and TB interactions in (**1**)–(**4**) reinforcing each other in the π* manifold.

Norbornadiene (1) is a prototypical molecule in which both through-space (TS) and through-bond (TB) interactions play an important role in determining the relative energies of the π_+ and π_- orbitals and of the π^*_+ and π^*_- orbitals.[1–9] In (1) the proximity of the double bonds results in TS interactions being more important than TB interactions in both π and π* manifolds. Assuming positive overlap between the basis π orbitals, (π_a and π_b), and between the basis π* orbitals, (π^*_a and π^*_b), direct TS interactions place the energy of the positive combination of π orbitals, $\pi_+[= 1/\sqrt{2}(\pi_a + \pi_b)]$ of a_1 symmetry, below that of the negative combination, $\pi_-[= 1/\sqrt{2}(\pi_a - \pi_b)]$ of b_1 symmetry (these definitions of π_+ and π_- only hold within the zero differential overlap approximation). Likewise, the energy of $\pi^*_+(b_2)$ lies below $\pi^*_-(a_2)$. Such a level sequence, *i.e.*, $E(\pi_-) > E(\pi_+)$ and $E(\pi^*_-) > E(\pi^*_+)$, where, for example, $E(\pi_+)$ represents the energy of the π_+ orbital, has been called the *natural* sequence of orbitals,[7] and always obtains for dominant TS interactions. This orbital sequence for (1) has been verified both theoretically[1–4] and experimentally, principally by electron transmission (ET) spectroscopy,[9] and photoelectron (PE) spectroscopy.[5,6] This is in contrast to cyclohexa-1,4-diene, in which TB interactions are more important than TS interactions. In this molecule, dominant TB interactions cause the occupied π levels (and apparently also the π* levels[8]) to have an *inverted* ordering, *i.e.*, $E(\pi_+) > E(\pi_-)$ and $E(\pi^*_+) > E(\pi^*_-)$.[1,5]†



(1) X = C
(2) X = Si
(3) X = Ge
(4) X = Sn



(5)

The properties of norbornadiene and its derivatives are of considerable interest due to the synthesis of rigid donor–acceptor compounds with repeated norbornyl groups as spacers, such as (5),[10,11e] and the subsequent demonstration that such spacers act as efficient mediators of long-range intramolecular electron transfer reactions.[11] Because of the importance of electron transfer processes,[12] and since TB coupling between the chromophores and the polynorbornyl sigma framework in molecules, such as (5) is clearly responsible for such efficacious electron transfer,[10] we have embarked on a theoretical program of research into ways of enhancing TB coupling in molecules in general, and in the norbornyl framework in particular. To this end, we have recently reported

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† Jordan *et al.*[9] originally concluded that the π* levels of cyclohexa-1,4-diene have a normal ordering. However, more recent experimental studies (T. M. Stevens and P. D. Burrow, unpublished results) and theoretical calculations (M. Falcetta and J. S. Y. Chao, and K. D. Jordan, unpublished results) provide strong evidence for an inverted sequence of π* levels.

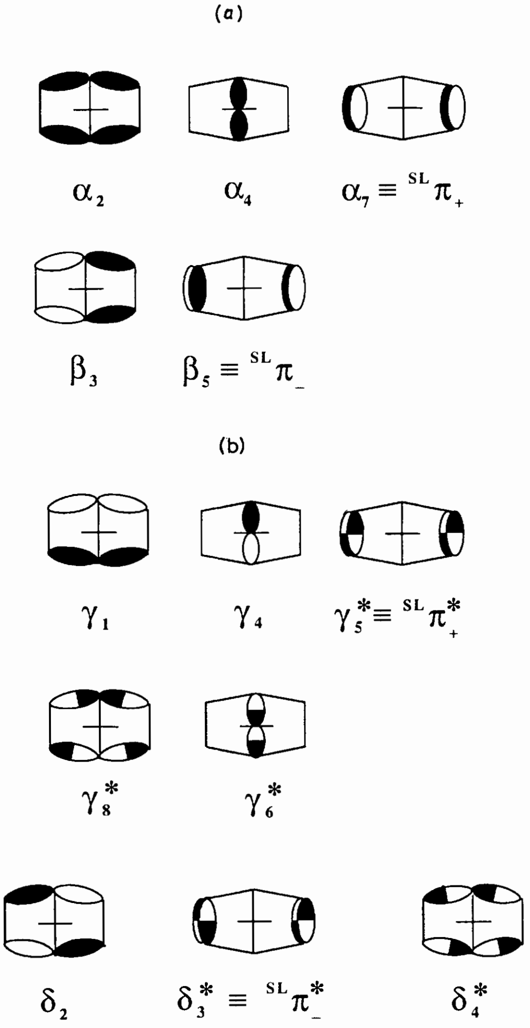

Figure 1. Sketches of some valence-shell SLMOs: (*a*) those having a_1 symmetry (the α set) and b_1 symmetry (the β set). (*b*) Those having b_2 symmetry (the γ set) and a_2 symmetry (the δ set). Virtual SLMOs are designated by asterisks.[4]

results of *ab initio* calculations on 7-silanorbornadiene (**2**), which show that the π levels in this molecule are very close in energy, but that they have an inverted sequence, *i.e.*, $E(\pi_+) > E(\pi_-)$.[13,14] Thus, replacement of the C-7 atom of norbornadiene by Si results in a switch in the relative importance of TB and TS interactions in the π manifold, with the former now being dominant [TS interactions still dominate in the π* manifold of (**2**), resulting in a natural sequence of π* orbitals].

A simple argument, based on the Heilbronner–Schmelzer analysis of orbital interactions,[4] has been advanced to explain the difference in the sequence of the π levels in (**1**) and (**2**),[13,14] and it goes as follows. The canonical molecular orbitals (CMOs) of (**1**) and (**2**) are transformed into a set of orthogonal localized (two centre) molecular orbitals (LMOs). From these localized orbitals, symmetry-adapted semi-localized MOs (SLMOs) are constructed, as detailed by Heilbronner and Schmelzer.[4] If, for the sake of simplicity, we restrict the basis set to the valence shell, then a total of 36 SLMOs may be formed there from, out of which twelve have a_1 symmetry and eight have b_1 symmetry (which are shown in full in refs. 4 and 14). The π_+ and π_- SLMOs are henceforth designated by ${}^{SL}\pi_+$ and ${}^{SL}\pi_-$ in order to distinguish them from the respective CMOs, π_+ and π_-. It has been demonstrated that π/σ mixing is energetically more important than π/σ* mixing, and consequently, the latter can be ignored.[14] There are six occupied σ SLMOs of a_1 symmetry $\{\alpha_i, i = 1,\ldots, 6\}$ that can mix with ${}^{SL}\pi_+(\equiv \alpha_7)$, and four of b_1 symmetry $\{\beta_j, j = 1,\ldots, 4\}$ that can mix with ${}^{SL}\pi_-(\equiv \beta_5)$. Moreover, it has been shown[4] that the σ SLMOs constructed from the CC bonds, namely, α_2, α_4, and β_3, make the major contributions to TB coupling in (**1**). These SLMOs together with the appropriate π SLMOs are shown in Figure 1(*a*). Both ${}^{SL}\pi_+$ and ${}^{SL}\pi_-$ levels are raised in energy through this mixing, although the former level is shifted more strongly than the latter because there is no counterpart to α_4 in the $\{\beta_j\}$ set of σ SLMOs.

Thus, TB interactions in (**1**) tend to place π_+ *above* π_-, although this tendency is outweighed by a stronger TS interaction in this molecule. However, replacement of C-7 in (**1**) by the larger (and more polarizable) Si atom substantially raises the self energy of the σ SLMO α_4, and also polarizes this orbital more towards C-1 and C-4. This follows from the fact that increasing the size of the atom X results in a lengthening of the A–X bond, and this in turn causes an increase in the energy of the filled σ orbital associated with the A–X bond, and to a corresponding decrease in the energy of the vitual σ* orbital (or, within the context of Koopmans' theorem, to a decrease in E_i and to an increase in E_{ea} of A–X, *vide infra*). Simple perturbational MO arguments suggest that such modifications to α_4, will lead to greater TB coupling involving π_+ in (**2**) compared with (**1**) and that this, in turn, will cause the energy of the π_+ (a_1) CMO level in (**2**) to be raised relative to that in (**1**). On the other hand, the energy of the π_- (b_1) CMO level, and hence, the degree of TB coupling involving this orbital, should be nearly the same in both (**1**) and (**2**) on account of the fact that X-7 makes no contribution either to the energy or to the polarization of the b_1 σ SLMO β_3. Apparently, the enhanced TB coupling to π_+ in (**2**) compared with (**1**), is sufficiently strong to result in an overall inverted sequence of π levels in the former molecule.[14]

It follows from this simple argument that substitution of C-7 by elements larger than Si, should lead to even stronger inversion of the π levels. We predict, therefore, that the degree of level inversion should increase along the series (**1**) < (**2**) (X-7 = Si) < (**3**)(X-7 = Ge) < (**4**)(X-7 = Sn), due largely to a progressive increase in destabilization of the π_+ (a_1) CMO. We also predict that the energy of the π_- (b_1) CMO should remain essentially constant along the series, for reasons given above. We now report the results of our *ab initio* MO SCF calculations on (**3**) and (**4**) which do, indeed, support these predictions.

Results and Discussion

All calculations were carried out using the GAUSSIAN 86 suite of programs.[15] Full geometry optimizations of (**1**)–(**4**) (C_{2v} symmetry constraint) were determined at the restricted Hartree–Fock (HF) level using the Schlegel analytical gradient procedure[16] and the STO-3G[17a–c] and STO-3G*[17d] basis sets. The latter set contains an additional set of polarization functions on the heteroatom. Although these basis sets are notably inflexible, previous calculations on (**1**) and (**2**) using a variety of basis sets, including split-valence shell basis sets, revealed that the STO-3G optimized geometries for these molecules are in good agreement with those obtained using more flexible basis sets.[12,13,18] Moreover, previous experience for norbornadiene and related compounds, has demonstrated that the STO-3G basis set, together with the assumption of Koopmans' theorem,[19] gives splittings between the π cation states and between the π* anion states in good agreement with experiment.[20] Accordingly, we believe, that the STO-3G and STO-3G* basis sets should also prove adequate for establishing

Table 1. HF/STO-3G and HF/STO-3G* optimized geometrical parameters[a] for the C_{2v} structures of **(1)**–**(4)**. The STO-3G* values are in parentheses.

Parameter	(1)	(2)	(3)	(4)
C(1)–X(7)	1.5560	1.8820 (1.8595)	1.9369 (1.9409)	2.1371 (2.1674)
C(1)–C(2)	1.5475	1.5426 (1.5404)	1.5449 (1.5431)	1.5428 (1.5405)
C(2)–C(3)	1.3110	1.3146 (1.3162)	1.3138 (1.3140)	1.3150 (1.3153)
C(2)–C(6)	2.4802	2.4630 (2.4770)	2.4606 (2.4722)	2.4535 (2.4617)
C(1)–H	1.0873	1.0831 (1.0835)	1.0833 (1.0847)	1.0835 (1.0847)
C(2)–H	1.0802	1.0809 (1.0814)	1.0809 (1.0813)	1.0814 (1.0815)
X(7)–H	1.0878	1.4247 (1.4284)	1.4345 (1.4847)	1.6311 (1.6841)
C(2)–C(1)–C(6)	106.52	105.94 (107.03)	105.57 (106.46)	105.34 (106.07)
C(1)–X(7)–C(4)	91.86	80.68 (82.80)	78.25 (78.74)	72.42 (71.80)
C(1)–C(2)–C(3)	107.39	111.32 (111.78)	111.46 (111.85)	113.09 (113.46)
H–C(1)–X(7)	118.11	123.16 (124.42)	123.27 (122.26)	125.10 (123.66)
H–C(2)–C(3)	128.76	126.44 (126.17)	126.44 (126.39)	125.43 (125.36)
H–X(7)–H	109.94	109.72 (109.10)	111.27 (110.04)	111.21 (110.03)
H–C(2)–C(3)–C(4)	177.81	178.44 (179.96)	177.91 (178.26)	177.96 (178.28)
φ	114.22	117.96 (119.96)	117.67 (119.31)	119.62 (121.15)

[a] Bond lengths in Å; bond angles and dihedral angles in degrees.

Table 2. HF/STO-3G//STO-3G and HF/STO-3G*//STO-3G* total energies[a] (E) for the C_{2v} structures **(1)**–**(4)**, together with the canonical π_+, π_-, π^*_+, and π^*_- MO energies[b] and their splitting energies,[c] Δ and Δ^*. The STO-3G* values are in parentheses.

	(1)	(2)	(3)	(4)
$-E^a$	266.42261	514.63280 (514.71006)	2 280.79199 (2 282.30345)	6 192.32466 (6 193.66020)
$\pi_-(b_1)^b$	−7.53	−7.42 (−7.67)	−7.38 (−7.64)	−7.18 (−7.42)
$\pi_+(a_1)^b$	−8.32	−7.25 (−7.18)	−7.12 (−7.29)	−6.31 (−6.47)
$\Delta^{b,c}$	0.79	−0.17 (−0.49)	−0.26 (−0.35)	−0.87 (−0.95)
$\pi^*_-(a_2)^b$	9.88	9.93 (9.55)	9.99 (9.70)	10.18 (9.92)
$\pi^*_+(b_2)^b$	8.12	8.23 (8.36)	7.97 (7.53)	7.51 (6.79)
$\Delta^{*\,b,c}$	1.76	1.70 (1.19)	2.02 (2.17)	2.67 (3.13)

[a] Energies in hartrees (1 hartree = 2 625 kJ mol^{-1}). [b] Orbital energies and splitting energies in eV (1 eV = 96.48 kJ mol^{-1}). [c] $\Delta = E(\pi_-) - E(\pi_+)$; $\Delta^* = E(\pi^*_-) - E(\pi^*_+)$. A negative sign for Δ means that the π_+ level lies energetically above the π_- level.

the qualitative trends in the relative energies of the π_+ and π_- orbitals for the series of molecules **(1)**–**(4)**. The HF/STO-3G and HF/STO-3G* optimized geometries for **(1)**–**(4)** are compared in Table 1 [for **(1)** the STO-3G* basis set is inapplicable, and only the STO-3G results are reported]. Total energies, π and π^* orbital energies, and splitting energies for **(1)**–**(4)** are given in Table 2. The splitting energies are defined by $\Delta = E(\pi_-) - E(\pi_+)$ and $\Delta^* = E(\pi^*_-) - E(\pi^*_+)$. A positive value for the splitting energy means that a natural sequence of orbitals obtains.

The geometries of **(2)**–**(4)** differ primarily from that of norbornadiene by having longer C–X and X–H bond lengths. One consequence of this difference is that the dihedral angle, φ, associated with the six-membered ring in **(2)**–**(4)** (*ca.* 118–120°) is *ca.* 4–6° larger than in **(1)**.[14] The C(1)–X(7) [and C(4)–X(7)] bond lengthens considerably, on going from **(1)** to **(2)** (by 0.3 Å) and from **(3)** to **(4)** (by 0.2 Å), but only moderately, on going from **(2)** to **(3)** (<0.1 Å). These results are consistent with trends in the atomic radii along the sequence C (0.914 Å), Si (1.32 Å), Ge (1.37 Å), and Sn (1.508 Å), where we see that, whereas Ge is only marginally larger than Si, Si and Sn are substantially larger than C and Ge, respectively. We also note that the calculations yield dipole moments for **(1)**–**(3)** which are quite small (*i.e.*, <0.3 D in magnitude), while that of **(4)** is found to be quite large (1.94 and 1.25 D, at the STO-3G and STO-3G* levels of theory, respectively).

The observed trends in the energies of the π_+ and π_- CMOs along the series **(1)**–**(4)** are in agreement with the above predictions derived from simple perturbational molecular orbital (PMO) theory. Thus, the energy of the π_- (b_1) CMO shows relatively little change along the series **(1)**–**(4)**. On the other hand, the π_+ (a_1) CMO is progressively destabilized along this sequence, with the STO-3G orbital energies being −8.32 **(1)**, −7.25 **(2)**, −7.12 **(3)**, and −6.31 eV **(4)** (see Table 2). Whereas Δ is positive (0.79 eV) for **(1)**, it is negative for **(2)**–**(4)**, being −0.17, −0.26, and −0.87 eV, respectively, using the STO-3G basis set. Interestingly, we observe a large increase in the energy of the π_+ CMO between **(1)** and **(2)** (*ca.* 1 eV), and between **(3)** and **(4)** (0.8 eV), but only a marginal increase is found between **(2)** and **(3)** (0.13 eV). This trend is also reflected in the change in the value of the splitting energy, Δ, along the series: −1 eV between **(1)** and **(2)**, −0.1 eV between **(2)** and **(3)**, and −0.6 eV between **(3)** and **(4)**. These trends parallel that already noted in the atomic radii along the series C, Si, Ge, and Sn (*vide supra*), and this is reasonable because the latter trend would lead one to expect large changes in energy between the C(1)–C(7)–C(4) and C(1)–Si–C(4) σ SLMO's, as well as between the C(1)–Si–C(4) and C(1)–Sn–C(4) σ SLMOs, but only a small change in energy between the C(1)–Si–C(4) and C(1)–Ge–C(4) σ SLMOs. This expectation is fulfilled by the observed trend in the first E_i along the series: $C(Me)_4$ (11.2 eV), $Si(Me)_4$ (10.4 eV), $Ge(Me)_4$ (10.2 eV), and $Sn(Me)_4$ (9.6 eV).[21]

A more quantitative insight into the interplay between TS and TB interactions in the series **(1)**–**(4)** was obtained using the procedure of Imamura *et al.*,[22a–e] which has already been applied to **(1)** and **(2)**.[14a] In this approach, one may begin with the Fock matrix in the basis of a suitable set of orthogonal LMOs in which *all* of the off-diagonal, but not the diagonal elements, have been set equal to zero. The diagonal elements of this 'blank' Fock matrix[22f] are the self-energies of the LMOs in

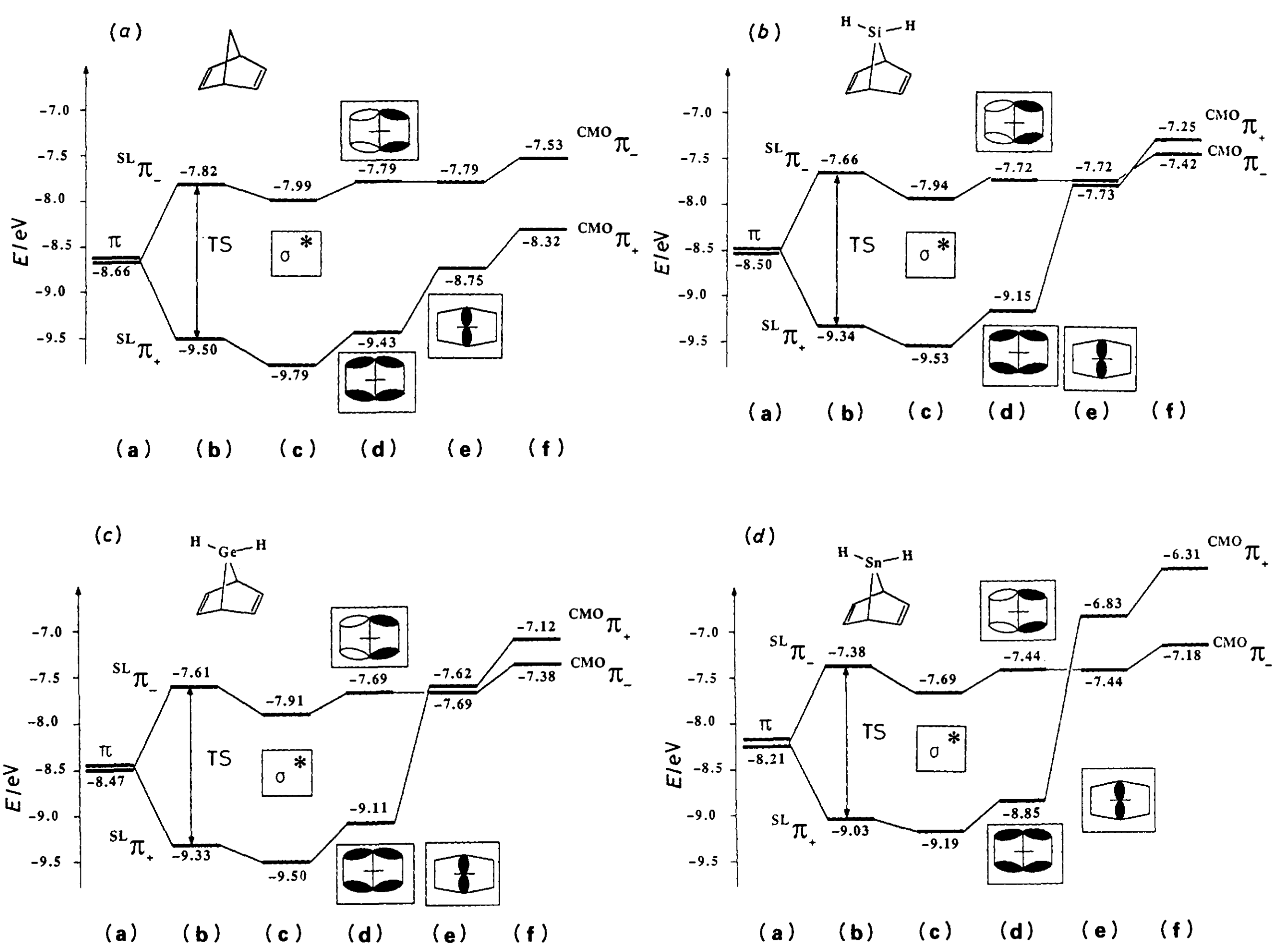

Figure 2. HF/STO-3G NBO interaction diagrams for the π orbitals of (*a*)(**1**), (*b*)(**2**), (*c*)(**3**), and (*d*)(**4**). The steps in each figure are as follows: (**a**) The two, degenerate, non-interacting localized π basis NBOs. (**b**) Inclusion of TS mixing between the two π basis NBOs generates the $^{SL}\pi_+(\equiv\alpha_7)$ and $^{SL}\pi_-(\equiv\beta_5)$ SLMOs. (**c**) Inclusion of TB interactions involving **all** σ* SLMOs. (**d**) Inclusion of TB interactions with α_2 and β_3 σ SLMOs. (**e**) Inclusion of TB interactions with α_4 σ SLMO. (**f**) Inclusion of **all** interactions, generating the CMOs $^{CMO}\pi_+$ and $^{CMO}\pi_-$ (Note: interactions with the core orbitals have also been included).

the absence of any TS and TB interactions. Orbital interactions are explored by progressively adding appropriate off-diagonal matrix elements to the blank Fock matrix and diagonalizing the resulting matrix at each step. The change in energy of a π-type orbital, resulting from mixing with a σ or σ* SLMO, is equated to the TB interaction energy between the two orbitals, and has a negative (positive) sign if the mixing leads to stabilization (destabilization) of π-type orbital.† We chose to use the Weinhold method of natural bond orbitals (NBOs)[23] for the orbital localization procedure, for reasons which have been discussed at length elsewhere.[13,14] The results for π orbital interactions in (**1**)–(**4**), which were obtained using the STO-3G basis set, are shown in Figure 2.‡

The TS splitting between the π LMOs [step (**b**) in Figure 2] is roughly the same for all four molecules and amounts to *ca.* 1.7 eV, which is considerably larger than the final splittings between the π CMOs. As expected,[14] the stabilization of the π_+ and π_- SLMOs, due to mixing with all the virtual σ* NBOs [step (**b**) ⟶ (**c**)] is quite small (≤ 0.3 eV); this is due to the large energy gap that separates the π levels from the σ* levels, as well as to the poor π,σ* overlap. Interestingly, and in complete agreement with simple theory (*vide supra*), the trend in the $\pi_-(b_1)$ level, as a function of the various TB interactions, is nearly the same for all four molecules. The major cause of the energy difference in the π_+ CMO level for the four molecules lies in the extent of TB coupling involving the α_4 σ SLMO (a_1 symmetry) which contains a contribution from X-7. Although the magnitude of the interaction between π_+ and the α_2 σ SLMO [*i.e.*, step (**c**) ⟶ (**d**)] is approximately constant along the series (*ca.* 0.37 eV), that between π_+ and the α_4 σ SLMO [step (**d**) ⟶ (**e**)] shows a substantial increase of 1.3 eV, upon going from (**1**) to (**4**). In agreement with simple arguments based on the trend in the atomic radii of C, Si, Ge, and Sn (*vide supra*), the greatest changes in the TB interaction energy between π_+ and α_4 take place on going from (**1**) to (**2**) (by 0.75 eV), and from (**3**) to (**4**) (by 0.53 eV), but with only a modest change upon going from (**2**) to (**3**) (by 0.06 eV). The interaction diagrams shown in Figure 2 clearly reveal the major role played by the α_4 σ SLMO in producing the calculated inverted sequence of π CMOs in (**2**)–(**4**).

We point out, however, that it is not possible to make an unambiguous quantitative partitioning of the net TB interaction energy between π_+ and the combined influence of the α_2 and α_4 σ SLMOs, into separate contributions from these orbitals, as implied by the discrete steps (**c**) ⟶ (**d**), and

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† Note that the TB interaction energy defined here is not equal to the total orbital splitting energy arising from the interaction. The latter quantity is defined as the energy gap separating the orbitals after mixing minus the energy gap separating the orbitals before mixing. For mixings involving orthogonal orbitals (as is the case for NBOs), the TB splitting is twice the TB interaction energy.

‡ In this analysis, interactions between all orbitals, including occupied core orbitals, have been taken into account.

Table 3. HF/STO-3G//STO-3G TB interaction energies eV between π_+ and π^*_+ orbitals with specified σ and σ^* SLMOs.[a,b]

	π_+		π^*_+		π^*_+	
	$\alpha_2 \longrightarrow \alpha_4$ $(\alpha_2 \longleftarrow \alpha_4)$		$\gamma_1 \longrightarrow \gamma_4$ $(\gamma_1 \longleftarrow \gamma_4)$		$\gamma^*_8 \longrightarrow \gamma^*_6$ $(\gamma^*_8 \longleftarrow \gamma^*_6)$	
(1)	0.36	0.68	0.18	0.28	−0.26	−0.51
	(0.80)	(0.24)	(0.24)	(0.22)	(−0.28)	(−0.49)
(2)	0.38	1.42	0.18	0.63	−0.26	−0.82
	(1.13)	(0.67)	(0.29)	(0.52)	(−0.20)	(−0.88)
(3)	0.39	1.49	0.18	0.62	−0.26	−1.12
	(1.19)	(0.69)	(0.29)	(0.51)	(−0.16)	(−1.22)
(4)	0.34	2.02	0.16	0.81	−0.26	−1.94
	(1.28)	(1.10)	(0.28)	(0.69)	(−0.06)	(−2.14)

[a] Non-parenthesized data refer to the mixing sequence A $\longrightarrow$ B, in which mixing with SLMO A precedes mixing with SLMO B, and parenthesized data refer to the reverse mixing sequence, that is, A $\longleftarrow$ B. [b] A negative (positive) value of TB interaction energy implies stabilization (destabilization) of the π_+ or π^*_+ orbital.

(d) $\longrightarrow$ **(e)** in Figure 2. This is because step **(d)** $\longrightarrow$ **(e)** includes not only the matrix element of interaction between π_+ and α_2, but also a matrix element of interaction between the α_2 and α_4 σ SLMOs.† If the matrix element of interaction between two σ SLMOs is small compared to the matrix elements resulting from interaction between each of these SLMOs with a π orbital of the same symmetry, then an unambiguous partitioning, as described above, is possible. If this situation does obtain, then the TB interaction energies associated with, say, the two steps **(c)** $\longrightarrow$ **(d)** and **(d)** $\longrightarrow$ **(e)**, must be independent of the order in which the mixings are carried out; that is, whether the sequence beginning with **(c)** $\longrightarrow$ **(d)** followed by **(d)** $\longrightarrow$ **(e)**, as shown in Figure 2, or with **(c)** $\longrightarrow$ **(e)** (*i.e.*, include α_4, but not α_2 interactions ‡), followed by **(e)** $\longrightarrow$ **(d)** (*i.e.*, include α_2 as well as α_4 interactions §) is immaterial. Although this is the case for the majority of the σ SLMOs associated with the norbonyl framework,[14] the matrix element of interaction between α_2 and α_4 is very large indeed [*ca.* −6 eV for **(3)**]. The resulting change in the energy of π_+ accompanying step **(d)** $\longrightarrow$ **(e)** is thereby increased by the presence of the interaction matrix element between α_2 and α_4, and this gives rise to an exaggerated contribution from α_4. Reversing these two steps would lead to different TB interaction energies associated with α_2 and α_4, although the combined TB interaction energy, resulting from mixing of π_+ with both α_2 and α_4, remains the same. This point is verified by the data in Table 3, in which π_+,α_2 and π_+,α_4 TB interaction energies are listed for the two possible mixing sequences, that is, mixing with α_2, followed by mixing with α_4 (non-parenthesized data), and the reverse sequence (parenthesized data). These data show that the TB interaction energy resulting from mixing with a particular SLMO (α_2 or α_4) is at least twice as large if the mixing with that SLMO is carried out subsequent to, rather than before mixing with the other SLMO.¶ Notwithstanding the ambiguity in assigning definite TB interaction energies to the π_+,α_2 and π_+,α_4 mixings,|| the results listed in Table 3 do show that, irrespective of the order in which these mixings are carried out, the energy change accompanying the mixing of π_+ with α_2 remains approximately constant along the series **(1)** $\longrightarrow$ **(4)** (*ca.* 0.4 eV for the sequence of mixings shown in Figure 2, and *ca.* 1.1 eV for the reverse sequence of mixings). This observation demonstrates that it is the bridge σ SLMO α_4, and not α_2, that plays the decisive role in determining the sequence of π CMOs in **(1)**–**(4)**.

We now comment on the trends in the π^* levels. The situation for π^* orbital interactions is a little more complicated than that for π orbital interactions since it has been found, both experimentally[20] and theoretically,[14a] that π^* orbitals mix significantly with both σ and σ^* orbitals. The relevant SLMOs are shown in Figure 1(*b*) (the virtual SLMOs are labelled with an asterisk). For all four molecules the two lowest unfilled CMOs are found to be $\pi^*_+(b_2)$ and $\pi^*_-(\alpha_2)$ with the π^*_+ being lower in energy. The energy of the π^*_- CMO is roughly constant for the four compounds (particularly at the STO-3G level of theory). The reason for this is similar to that advanced to explain the constancy of the π_- energy level along the series **(1)**–**(4)**, namely, that the σ and σ^* SLMOs of a_2 symmetry that mix with $\delta^*_3(\equiv{}^{SL}\pi^*_-)$, do not contain any significant contribution from X-7.†† The calculations also indicate that the b_2 π^*_+ CMO is slightly destabilized in **(2)**, relative to **(1)**, while in **(3)** it is slightly stabilized. However, this orbital is strongly stabilized in going from **(3)** to **(4)**. The reason for the sensitivity of the π^*_+ to the nature of X-7 is that it, unlike π^*_-, can mix with the bridge γ_4 σ SLMO and γ^*_6 σ^* SLMO [Figure 1(*b*)]. As one progresses along the series, **(1)** $\longrightarrow$ **(4)**, the mixing of π^*_+ with both γ_4 and γ^*_6 is expected to increase. This is due to the increasing energy of γ_4 and the decreasing energy of γ^*_6 as X descends the Periodic Table. The trends in the E_i values of the X(Me)$_4$ molecules were noted above. ET spectroscopic studies give the following values for the EA's of these molecules: C(Me)$_4$ (−6.1 eV), Si(Me)$_4$ (−4.1 eV), Ge(Me)$_4$ (−3.7 eV), Sn(Me)$_4$ (−2.9 eV).[21] Our calculations further indicate that π^*_+,γ^*_6 mixing becomes progressively more important than π^*_+,γ_4 mixing as X descends the Periodic Table, thereby resulting in the increasing stabilization of the π^*_+ CMO level. Indeed, the π^*_+,γ^*_6 mixing becomes so strong in **(4)** that the so-called b_2 π^*_+ CMO contains only *ca.* 50% C=C π^* character. In fact, there is a second b_2 virtual CMO in **(4)**, lying <1 eV above that of the a_2 π^*_- CMO, which also contains considerable C=C π^* and C–Sn–C σ^* character.

A quantitative dissection of π^* orbital interactions was carried out, and the results are shown in Figure 3. The π^*,π^* TS interaction energy is constant along the series, as was found to be the case for the corresponding π,π interaction energy, although we note that the magnitude of the former (*ca.* 1.5 eV) is slightly smaller than that of the latter (*ca.* 1.7 eV), for reasons that have been discussed elsewhere.[14]

The energy diagrams of Figure 3 show that TB coupling to the $\pi^*_-(a_2)$ orbital is fairly weak and that the π^*_-,σ and π^*_-,σ^* interactions have comparable magnitudes which nearly cancel

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† To be exact, step **(d)** $\longrightarrow$ **(e)** includes all interactions between α_4 and the σ and σ^* SLMOs that are associated with the preceeding steps, **(b)** $\longrightarrow$ **(c)** $\longrightarrow$ **(d)**. However, only the α_4,α_2 interaction is energetically significant.

‡ Together with interactions between α_4 and all other σ SLMOs that were included in step **(b)** $\longrightarrow$ **(c)**.

§ Together with interactions between α_2 and all other σ SLMOs that were included in preceding steps.

¶ Additional calculations show that the ambiguity in partitioning TB interaction energies is restricted only to the mixing of π_+ with α_2 and α_4 SLMOs. Thus the same pattern on TB interaction energies emerge if the mixing of π_+ with the set of σ SLMOs is carried out before its mixing with the σ^* SLMOs, rather than the other way round, as shown in Figure 2.

|| This problem can be avoided by mixing the α_2 and α_4 σ SLMOs, to form two new a_1 orbitals, termed 'pre-canonical molecular orbitals' (PCMOs) by Heilbronner and Schmelzer.[4] These PCMOs are then separately interacted with the π_+ orbital to get the respective TB interaction energies (note that the matrix element of interaction between two PCMOs is zero[4]).

†† For calculations using minimal basis sets, such as STO-3G, X-7 does not have any basis orbitals of a_2 symmetry. Consequently, at this level of theory, the π^*_- CMO cannot contain any contribution from the X-7 atom. However, inclusion of polarization functions at X-7 (such as using the STO-3G* basis set) does, in principle, allow such a contribution to be made although it is energetically quite small.

each other out, owing to their opposite signs. The major contributors to the π_-^* TB interactions stem from mixing with the SLMOs δ_2 [step (**b**) ⟶ (**c**)], which destabilizes π_-^*, and δ_4^* [step (**e**) ⟶ (**f**)], which stabilizes π_-^*, by nearly the same amount (*ca.* 0.25 eV). These interaction energies have the same magnitude for all four molecules. Turning to TB interactions with π_+^*, we find that they are stronger than those involving π_-^*. The relative contributions of the γ_1 and γ_4 σ SLMOs, and the γ_6^* and γ_8^* σ^* SLMOs, are given in Figure 3. Whereas, not unexpectedly, both π_+^*,γ_1 and π_+^*,γ_8^* interaction energies are small, and nearly constant for all four molecules (*i.e.*, 0.18 eV for the former and −0.26 eV for the latter), such is not the case for the π_+^*,γ_4 and π_+^*,γ_6^* interaction energies, which increase substantially with increasing atomic number of X-7 (see Table 3). In addition, it is seen that the π_+^*,γ_6^* interaction energy is greater than the π_+^*,γ_4 interaction energy in each of the four molecules, and that this difference increases with increasing atomic number of X-7. These findings hold irrespective of the order in which the mixings are carried out, as borne out by the data of Table 3. The most likely reason for this is that the absolute values of the matrix elements for interaction between γ_1 and γ_4, and between γ_6^* and γ_8^* (*ca.* 4.0 and 0.3 eV, respectively) are smaller than the matrix element between α_2 and α_4 (*vide supra*). Finally, we note that, for all four molecules studied here, π_+^*,σ^* interactions are more important than π_+^*,σ interactions.

Although we must exercise caution in using bound state calculations, such as those employed herein, to characterize unfilled orbitals (or anion states) embedded in the continuum, the results appear to be consistent with the trends in the experimentally observed E_i and E_{ea} along the X(Me)$_4$ series of molecules. However, experimental studies will be required to determine whether the two lowest anion states of (**3**) and (**4**) are appreciably more split than are the lowest two anion states of (**1**) and (**2**).

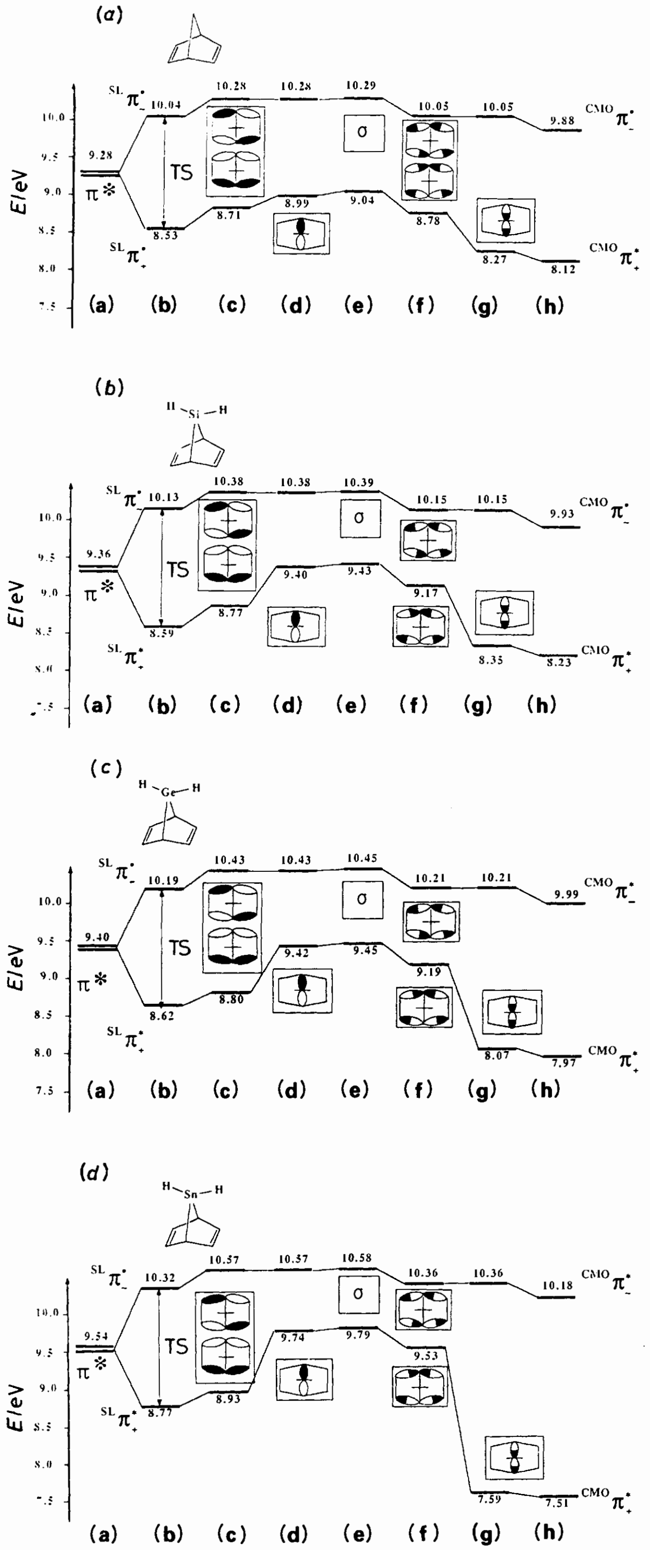

Figure 3. HF/STO-3G NBO interaction diagrams for the π^* orbitals of (*a*)(**1**), (*b*)(**2**), (*c*)(**3**), and (*d*)(**4**). The steps in each figure are as follows: (**a**) The two, degenerate, non-interacting localized π^* basis NBOs. (**b**) Inclusion of TS mixing between the two π basis NBOs generates the $^{SL}\pi_+^*(\equiv\gamma_5^*)$ and $^{SL}\pi_-^*(\equiv\delta_3^*)$ SLMOs. (**c**) Inclusion of TB interactions with γ_1 and δ_2 σ SLMOs. (**d**) Inclusion of interactions with γ_4 σ SLMO. (**e**) Inclusion of TB interactions involving **all** σ SLMOs. (**f**) Inclusion of interactions with γ_8^* and δ_4^* σ^* SLMOs. (**g**) Inclusion of interactions with γ_6^* σ^* SLMO. (**h**) Inclusion of **all** interactions, generating the CMOs $^{CMO}\pi_+^*$ and $^{CMO}\pi_-^*$.

Conclusions

The present theoretical calculations show that (**3**) and (**4**), like (**2**), have an inverted sequence of π levels, with the π_+,π_- splitting increasing along the sequence (**2**)–(**4**). A quantitative dissection of the TS and TB interaction energies in (**1**)–(**4**) was carried out using NBOs as the localized basis orbitals within the framework of the Imamura scheme. This analysis clearly reveals the important role played by the bridge C(1)–X(7)–C(4) σ SLMO,α_4, in determining the ordering of the π CMO levels. The π^* levels, on the other hand, are found to have the 'natural' ordering for all molecules. Furthermore [with the exception of (**2**)] the calculated π_+^*,π_-^* CMO splitting increases with increasing atomic number of X-7, attaining the substantial value of 2.7 eV for (**4**), and this is largely due to concomitant increasing stabilization of the π_+^* level. These results imply, then, that π_+^*,σ^* interactions are more important than π_+^*,σ interactions. An Imamura type analysis of interactions involving the π_+^* orbitals supported this implication.

With respect to experimental verification of these predictions, it is expected that the parent compounds (**2**)–(**4**) should be extremely unstable. Indeed, they have yet to be detected experimentally. The 7,7-dimethyl derivatives of (**2**)–(**4**) would probably prove more suitable than the 'parent' compounds studied here, and it is heartening to note that some, albeit highly substituted, derivatives of (**2**),[24] (**3**),[25] and (**4**)[26] are known. In our earlier theoretical study of (**2**),[14] the 7,7-dimethyl derivative of this molecule was also examined. These calculations gave similar results for the π and π^* splittings for both (**2**) and its 7,7-dimethyl derivative. We expect that the 7,7-dimethyl derivatives of (**3**) and (**4**) would also have π and π^* splittings comparable to those of the parent molecules studied here.

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