An *Ab Initio* M.O. Study of 7-Silanorbornadiene and 7,7-Dimethyl-7-silanorbornadiene; Examples of Norbornadienes in which the π Orbitals interact largely through-bonds rather than through-space

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It has been found that the π M.O.s of the fully optimized title molecules (HF/3-21G, C_{2v} symmetry constraint) follow an inverted sequence [*i.e.* the π_+ (a_1) level lies above the π_- (b_1) level]; a Natural Bond Orbital (N.B.O.) analysis reveals the origin of this inverted sequence.

Norbornadiene, (**1a**) has become a paradigm for a molecule that exhibits dominant through-space (TS) orbital interactions within both π and π^* manifolds.[1—6] This is a consequence of the structurally enforced propinquity of the double bonds in (**1a**), due largely to the small value of the dihedral, ϕ, of 112°,[7] associated with the six-membered ring. TS interactions result in the levels of the (fully delocalized) π and π^* canonical M.O.s (C.M.O.s) following the natural sequence,[4] *i.e.*, $E(\pi_-) > E(\pi_+)$ and $E(\pi^*_-) > E(\pi^*_+)$ [where π_+ (π^*_+) represents the symmetric combination of π (π^*) basis orbitals with respect to the plane passing through C-1, C-7, and C-4 of (**1a**), and π_- (π^*_-) the corresponding antisymmetric combination]. This orbital sequence for (**1a**) has been verified both theoretically[1,3,4] and experimentally, by photoelectron spectroscopy,[5] and by electron transmission (E.T.) spectroscopy.[6]

However, semi-empirical M.O. calculations[3,4] on (**1a**) also indicate the presence of through-bond (TB) interactions[2,8] between the π orbitals which oppose the TS interactions and which, by themselves, would result in an inverted sequence[4] of π levels [*i.e.*, $E(\pi_+) > E(\pi_-)$]. Although TS interactions are stronger than TB interactions in (**1a**), it is of interest to inquire whether the relative importance of these interactions can be reversed in a suitably modified norbornadiene. We report that such is the case for 7-silanorbornadiene, (**1b**), and its

7,7-dimethyl analogue, (**1c**). The structures for (**1a**)[9]—(**1c**) were fully optimized (within C_{2v} symmetry constraint) at the Hartree–Fock level using the STO-3G, 3-21G, and 3-21G(*) basis sets (the latter contains a set of d functions on the Si atom).[10] The calculations were performed with the GAUSSIAN 82 suite of programs.[11] Optimized values of some salient geometric parameters, using the 3-21G basis set, for (**1a**)—(**1c**) are given in Table 1, together with the energies of the canonical π and π^* M.O.s (*i.e.*, π_-, π_+, π^*_-, and π^*_+) and the corresponding splitting energies, $\Delta = E(\pi_-) - E(\pi_+)$, and $\Delta^* = E(\pi^*_-) - E(\pi^*_+)$. A positive value for the splitting energy means that a natural sequence of orbitals obtains. Whereas Δ for (**1a**) is positive, thereby indicating a natural sequence of π levels in this molecule, it is negative for both (**1b**) and (**1c**). Calculations using the STO-3G and 3-21G(*) basis sets give values of Δ for (**1a**), (**1b**), and (**1c**) which are within 0.02 eV of the 3-21G result. This insensitivity of Δ to the basis set reinforces our belief that the level inversion calculated for (**1b**) and (**1c**) is genuine. However, the π^* levels for (**1b**) and (**1c**) still follow the natural sequence, and so TS interactions remain dominant here.

The reversal of the relative importance of TS and TB interactions in (**1b**) and (**1c**), compared to (**1a**), is attributed to a combination of geometric and electronic factors. The geometric factor derives from the rapid attenuation of the TS interactions with increasing value of ϕ, as a result of diminishing π,π orbital overlap.[3,4,5c] Because TB effects are less sensitive to ϕ (the loss in overlap of the π M.O.s with the σ orbitals of the six-membered ring, with increasing ϕ, is compensated by a corresponding gain in overlap with the C1–X7–C4 bridge σ orbitals), there should be a value for ϕ for which TB interactions become dominant. MINDO/2 calculations predict this to occur in (**1a**) at $\phi \approx 116°$.[3] In the present study, the geometrical factor was explored by carrying out a series of single point 3-21G calculations on (**1a**) and (**1b**) for different values of ϕ. Unlike the MINDO/2 result,[3] the 3-21G π_- and π_+ levels for (**1a**) follow the natural sequence over the entire range of values of ϕ studied (114°—124°), whereas for (**1b**), the calculated crossover value for ϕ is *ca.* 118°. Thus, the inverted sequence of π levels found for (**1b**) and (**1c**) is due in part to the somewhat larger equilibrium value of ϕ for these molecules, compared to (**1a**); if the value of ϕ for (**1b**) and (**1c**) happened to be similar to that found for (**1**) (114°), a TS dominated Δ value of *ca.* 0.46 eV would then result. The fact that the crossover value of ϕ for (**1a**) is much larger than that for (**1b**) suggests that TB interactions in (**1a**) must be substantially weaker than in the latter molecule.

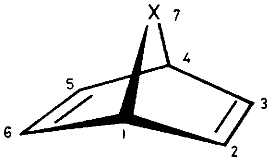
The electronic factor influences TB interactions and may be illustrated using the following simple argument. There are three symmetry-adapted semi-localized M.O.s (σ-S.L.M.O.s) that are particularly relevant to TB coupling in the norbornyl system,[4] and these are shown schematically by (**2**)—(**4**). Arguments based on symmetry reveal that both (**2**) and (**3**) can mix with π_+, and that (**4**) can mix with π_-. Both π_+ and π_- levels are thereby raised through this σ/π mixing, although the former should be more affected than the latter because there is no σ-S.L.M.O. counterpart to (**3**) that can mix with π_-. Thus, TB interactions in (**1**), by themselves, lead to an inverted sequence of π levels. Although replacement of C-7 in (**1**) by Si should have little effect on the energies and shapes of (**2**) and (**4**) (X-7 makes no contribution to these orbitals), the self-energy of orbital (**3**) should be raised by such substitution (*i.e.*, Si is more electropositive than C). Consequently, because of the narrower energy gap that obtains between π_+ and the σ-S.L.M.O. (**3**) in (**1b**), relative to (**1a**), TB coupling with π_+ is larger in (**1b**), compared to (**1a**). Net TB interactions, *i.e.*, the difference between the π_- and π_+ levels resulting exclusively from TB effects, should, therefore, be larger for (**1b**) [and (**1c**)] than for (**1a**).

The above reasoning can be quantified by dissecting the net orbital interactions into TS and TB components along the lines suggested by Heilbronner and Schmelzer.[4] The Weinhold natural bond orbital (N.B.O.)[12,13] procedure was used to

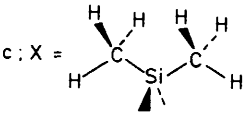
Table 1. HF/3-21G optimized geometrical parameters[a] and energies[b] (E) for the C_{2v} structures (**1a**)—(**1c**), together with the canonical π_+, π_-, π^*_+, and π^*_- M.O. energies[c] and their splitting energies,[c] Δ and Δ^*.

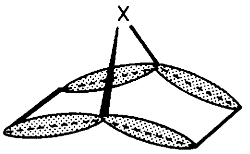
Parameter	(**1a**)[d]	(**1b**)	(**1c**)
C-1–X-7	1.566	1.949	1.961
C-1–C-2	1.550	1.539	1.536
C-2–C-3	1.319	1.325	1.325
C-2–C-6	2.480	2.474	2.467
C-8–Si			1.911
C-2–C-1–C-6	106.2	107.0	106.9
C-1–X-7–C-4	92.0	79.1	78.4
C-1–C-2–C-3	107.5	112.1	112.1
C-8–SI–C-9			108.3
ø	114.0	120.4	120.3
$-E$	268.16187	517.91532	595.60065
$E(\pi_-)$	−8.72	−9.04	−8.83
$E(\pi_+)$	−9.76	−8.88	−8.62
Δ[e]	1.04	−0.16	−0.21
$E(\pi^*_-)$	6.28	5.84	5.93
$E(\pi^*_+)$	4.29	3.39[f]	4.23[f]
Δ^*[e]	1.99	2.45	1.69

[a] Bond lengths (Å), bond and dihedral angles (°). [b] Energies in a.u. (1 a.u. = 2625.5 kJ/mol). [c] Orbital energies and splitting energies in eV (1 eV = 96.48 kJ/mol). [d] See also ref. 9. [e] $\Delta = E(\pi_-) - E(\pi_+)$; $\Delta^* = E(\pi^*_-) - E(\pi^*_+)$. A negative sign for Δ means that the π_+ level lies above the π_- level. [f] There is another orbital of b_2 symmetry *ca.* 2.4 eV higher in energy in both (**1b**) and (**1c**). Both b_2 orbitals result from strong mixing of π^*_+ with the C1–Si–C4 σ^* b_2 orbital.

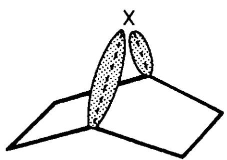


(**1**) a; X = CH_2
b; X = SiH_2
c; X =

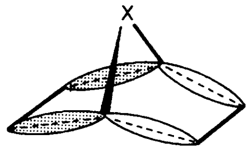




(**2**)



(**3**)



(**4**)

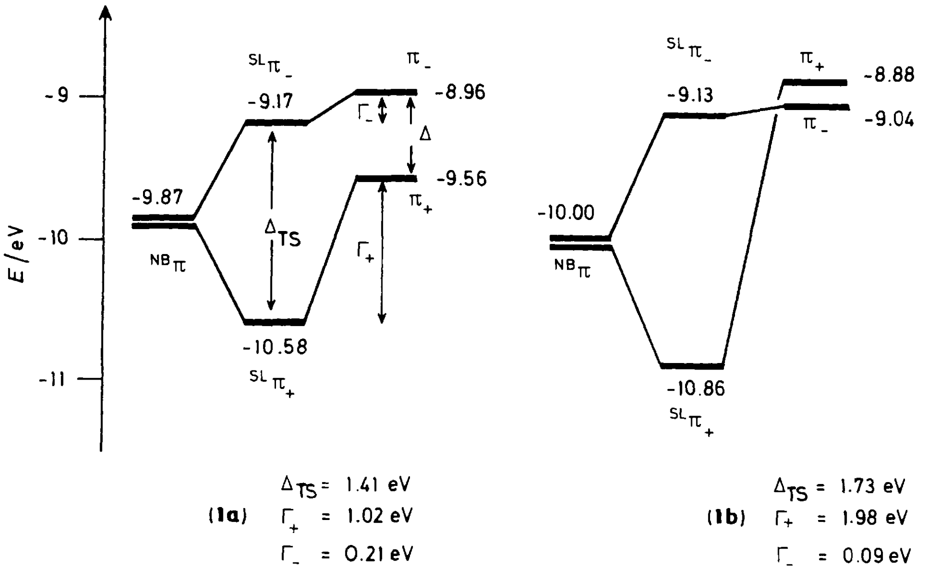


Figure 1. N.B.O.[12,13] interaction diagrams for (**1a**) and (**1b**) for $\phi = 120°$. $^{NB}\pi$ is the π NBO; $^{SL}\pi_+$ and $^{SL}\pi_-$ are the semi-localized symmetry-adapted combination of the two $^{NB}\pi$ basis orbitals, and Δ_{TS} is the TS interaction energy; π_+ and π_+ are the final (fully delocalized) C.M.O.s, with Δ the net splitting energy from combined TS and TB interactions. Γ_+ and Γ_- are the total TB contributions to π_+ and π_-, respectively.

obtain the localized π basis levels ($^{NB}\pi$) in (**1a**) and (**1b**), together with the pure TS splitting energies, Δ_{TS} between the two $^{NB}\pi$ basis orbitals in each molecule. The π orbitals resulting from these TS interactions are the π-S.L.M.O.s, $^{SL}\pi_+$ and $^{SL}\pi_-$. The energy difference between $^{SL}\pi_+$ and $^{SL}\pi_-$ and the respective final canonical orbitals, π_+ and π_-, gives the total TB contribution (Γ_+ and Γ_-) to each C.M.O. In this way, the two interaction diagrams for (**1a**) and (**1b**) were constructed (Figure 1) for φ set equal to that found for optimized (**1b**) (*i.e.*, 120°). As expected, Δ_{TS} is comparable for both molecules and is substantially larger than the net splitting energies, Δ. In complete agrement with the above qualitative reasoning, Γ_- is considerably smaller than Γ_+ for both (**1a**) and (**1b**), and, more importantly, Γ_+ for (**1b**) is almost 1 eV larger than that for (**1a**). It is this large value of Γ_+ for (**1b**) that is primarily responsible for the π level inversion in this molecule. We find that, although Γ_+ and Γ_- remain unaltered, Δ_{TS} for (**1b**) rapidly increases with decreasing φ until, for $\phi < 118°$, $\Delta_{TS} > (\Gamma_+ - \Gamma_-)$ and TS effects now dominate. For (**1a**), Γ_+ is not quite large enough to cause level inversion, even for $\phi = 120°$; we predict this to occur for $\phi > 130°$.

Interestingly, the π* levels in (**1b**) and (**1c**) follow the natural sequence, even if φ is increased to 124°. Presumably,TB coupling of π^*_+ with the σ relays is not strong enough to overcome the TS interactions. This is understandable when it is recognized that TS interactions may be larger between π* orbitals than between π orbitals (the former are more diffuse and therefore overlap better with each other), and also that σ/π* TB should be weaker than σ/π interactions (the σ/π* energy gap is greater than the σ/π energy gap).

Our predictions are subject to experimental verification. Since analogues of (**1c**) are known and are reasonably stable,[14] the synthesis of (**1c**) should be achievable and constitute a worthwhile goal.

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