

Does π - σ - π Through-Bond Coupling Significantly Increase C–C Bond Lengths?

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Abstract: Orbital effects ascribed to π - σ - π through-bond coupling are the result primarily of destabilizing filled–filled interactions; little to no mixing occurs between the antisymmetric π combination and σ^* . The magnitude of through-bond coupling does not correlate with bond lengthening. Previous conclusions that through-bond coupling induces long bonds relied in some cases on poor X-ray data and/or inappropriate molecular orbital theories to deduce geometries. Comparison of semiempirical and empirical force field data as a test for through-bond coupling is unwarranted. Standard force fields underestimate the steric bulk of the benzene face, but addition of so-called “through-bond coupling” terms does not provide a physically significant measure of through-bond coupling.

Although carbon–carbon bond lengths cover a broad range of values (1.2–1.7 Å), chemists associate specific bond lengths with specific bond types (e.g., C_{sp^3} – C_{sp^3} = 1.54 Å; C_{sp^2} – C_{sp^2} = 1.33 Å; C_{sp} – C_{sp} = 1.21 Å).² Because of the tight distribution of experimental observations around these foci, significant deviations from these “standard” values are often diagnostic of novel steric or electronic features. Once understood, these features provide the basis for empirical structure prediction.³ Through-bond coupling,^{4,5} the mixing of “lone p” or π orbitals through the intervening σ skeleton, is one such electronic feature proposed to have strong and predictable geometrical ramifications on bond lengths,^{6–12} however, the exceptional experimental geometries and the original level of theory upon which this proposal had been made are now called into question.¹³ The present work focuses on the details of 1,4 orbital interactions as a combination of through-bond and through-space effects, and points out how the effects from strongly electronically-coupled systems can, nonetheless, be geometrically cryptic.

Through-Space vs Through-Bond Interactions

Orbital Effects. When two degenerate orbitals interact through space, two combination orbitals are formed: a higher

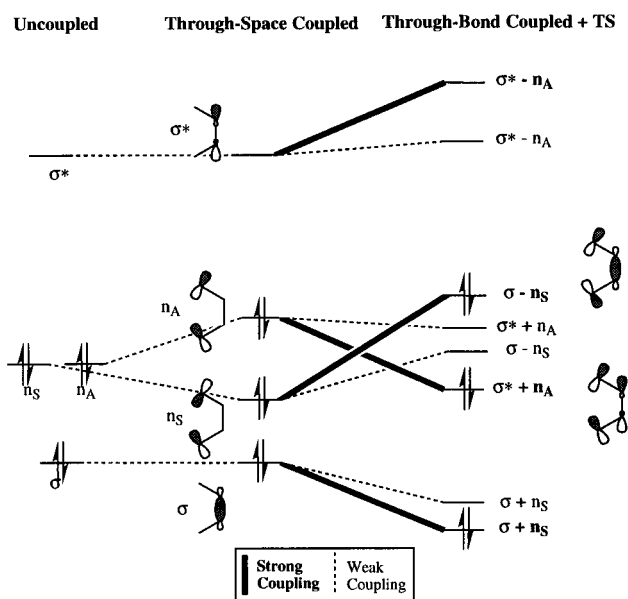


Figure 1. Orbital interaction diagram showing through-space and through-bond effects.

energy antisymmetric form ($A = p_1 - p_2$) and a lower energy symmetric form ($S = p_1 + p_2$) (Figure 1). For first-row elements at bonding distances (i.e., ca. 1.5 Å) the energy splitting $\Delta E = (E_A - E_S)$ is ca. 4 eV (ca. 90 kcal/mol). At distances greater than 3.0 Å, the energy splitting is reduced to less than 0.5 eV (11–12 kcal/mol). When both orbitals are doubly occupied, such orbitals would be considered nonbonding but through-space coupled, and ΔE is a quantitative measure of that coupling. If the orbitals are connected by three σ bonds as in diazabicyclo[2.2.2]octane (**1**), the possibility arises for the nonbonding pair of orbitals to couple through the central σ and σ^* orbitals. In the case where coupling to the central σ bond plays a dominant role, the ordering of the energy levels switches such that S is higher in energy than A; thus, the order of S to A is a convenient diagnostic of the type and relative magnitude of coupling.

In the 1960s, Hoffmann and co-workers examined “lone pair” or nonbonding orbital interactions over intervening σ bonds with

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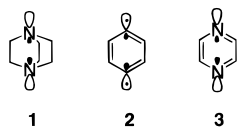
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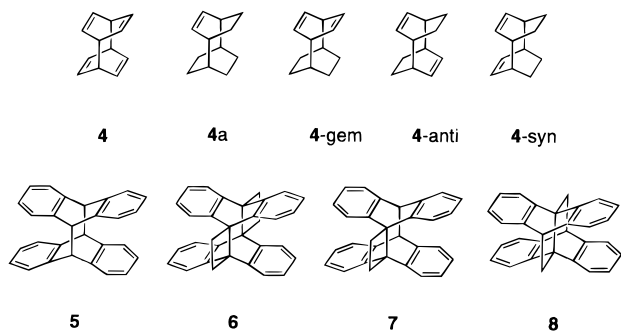
extended Hückel theory calculations (EHT)⁴ for **1**, *p*-benzyne (**2**), and pyrazine (**3**). EHT analysis predicted a substantial (>1



eV) splitting in the calculated levels with S ($\sigma - S$ in Figure 1) higher in energy than A ($A + \sigma^*$ in Figure 1). This orbital interaction was later confirmed experimentally in **1**^{14,15} and **2**,¹⁶ using photoelectron spectroscopy.

The concept of $n-\sigma-n$ through-bond coupling was introduced to address the orbital splitting seen for **1**–**3**. In these three structures, the long axis of the central σ bond is aligned with the long axes of the nonbonding orbitals. Interactions of σ with S and σ^* with A provide a simple first-order rationale for the unexpectedly large splitting and ordering of the orbitals; these interactions can raise the energy of the molecular orbital derived from $\sigma - S$ and/or lower the corresponding $\sigma^* + A$ energy. The $\sigma - S$ interaction is a filled–filled interaction that leads to a net destabilization of the molecule, but does not support a clear prediction for structural distortion of the central bond. In contrast, the $\sigma^* + A$ interaction is a net stabilizing interaction with distinct geometrical ramifications. The bond order of the central bond is predicted to decrease and the bond should weaken, whereas the flanking bonds should have a strengthened π bonding interaction and increase in bond order. Thus, the qualitative structural predictions are a lengthened central bond and shortened flanking bonds.⁵ Although the precise magnitude of these structural distortions is inaccessible by EHT methods, one can be sure that, in the absence of substantial $\sigma^* + A$ mixing, predictions of large geometrical changes are unwarranted.

Although the orbital concepts of $n-\sigma-n$ through-bond coupling were not directly linked to geometrical distortions, $\pi-\sigma-\pi$ through-bond coupling was invoked specifically to explain anomalous molecular geometries such as the long bonds observed in *p*-dibenzene and cognates (**4**–**8**).^{6–12} It was



assumed that the π systems of **4** and related compounds will act in lieu of nonbonded orbitals. If this assumption were valid, such through-bond effects should be present in a wide variety of molecules, from the commercially available 1,2-diphenylethane (**9**) to the as yet unsynthesized **4**. The molecular orbital diagram may appear unresolvable in some cases; however, when the choice of interacting orbitals is limited by symmetry, the diagram is simplified. As such, it is possible to dissect rough through-bond and through-space splitting energies from comparison of experiments like photoelectron spectroscopy with ab

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Table 1. Central Bond Lengths (Å) and Orbital Energies (eV) for **4**–**27**

	central	HOMO	HOMO - 1	HOMO - 2	HOMO - 3
4	1.631	-7.8	-9.2	-9.9	-10.0
4a	1.583	-9.1			
<i>gem</i> - 4	1.594	-8.9	-9.4		
<i>syn</i> - 4	1.597	-8.8	-9.4		
<i>anti</i> - 4	1.584	-8.7	-9.9		
4(F)	1.635	-9.0	-10.8	-11.3	-11.3
5	1.625 ^a				
5(F)	1.631 ^a				
6	1.635	7.7	-8.4	-8.5	-8.7
7	1.638	-7.6	-8.5	-8.5	-8.5
8	1.623	-8.0	-8.4	-8.7	-8.7
9a	1.542	-8.6	-8.9	-9.0	-9.0
9s	1.570	-8.5	-8.7	-8.7	-9.0
10	1.602	-7.8	-7.9	-8.4	-9.6
11	1.615	-9.2	-9.3	-10.6	-10.8
12	1.532				
13	1.578 ^a				
14	1.568 ^a (1.567)	-8.4	-8.5	-8.8	-8.9
15	1.577 ^a				
16	1.557 ^a				
17	1.54 ^a				
18	1.56 ^a (1.56)				
19	1.630				
20	1.604	-7.3	-7.7	-8.7	-8.9
21	1.606	-7.8	-9.2	-9.4	-9.7
22	1.606	-9.5	-9.9	-10.1	-10.1
23	1.604	-8.2	-8.8	-8.8	-9.0
24	1.559/1.595	-10.9	-11.6	-11.8	-11.9
25	1.553/1.57	-11.2	-11.9	-12.0	-12.1
26	1.553	-8.9	-10.1	-10.8	-11.2
27	1.577	-9.1	-9.5	-10.6	-11.6

^a X-ray data (**5**, Choi, C. S.; Marinkas, P. L. *Acta Crystallogr.* **1980**, B36, 2491; **5(F)**, ref 12; **13**–**18**, refs 44 and 45).

initio molecular orbital calculations. Comparison of these splitting energies with molecular geometries reveals two important facts: (1) *through-bond splitting is dominated by filled–filled interactions which are destabilizing*,^{17–24} and (2) *the magnitude of through-bond coupling does not correlate with changes in central bond length*.

Computational Methods

Ab initio calculations have been carried out (Table 1) to predict geometries and orbital energy trends using restricted Hartree–Fock (RHF) techniques with the aid of analytically determined gradients and the search algorithms contained within GAMESS,^{25,26} using the 6-31G(d),²⁷ DZV(md,np),²⁸ and TZV(md,np)²⁹ basis sets ($m = 1, 2; n = 0, 1$). A tight SCF convergence criterion (10^{-6} au) was used for the

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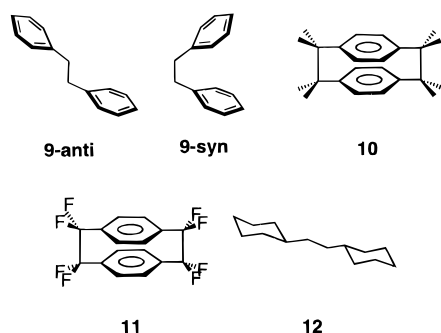
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SCF calculation, and an RMS gradient convergence criterion of less than 0.0003 au was specified.

The assignments of orbital energies in this study have been based on the theorem of Koopmans.³⁰ The approximations inherent in this theorem (reorganization vs correlation energy and basis set effects) make it difficult to compare directly these calculated values with the observed vertical ionization potentials (IP's),^{31–34} however, it has been shown³³ that even if the energies themselves are not directly comparable to observed values with the accuracy needed for assignment, Koopmans' theorem values are generally able to reproduce the variations of the IPs along the series of molecules. Taking this into account, we use the calculated values at the specified levels of theory for a series of similarly constructed molecules, carefully checking both the basis set dependence tests and the comparison to available experimental data to ensure that the order of the levels has been properly assigned. Comparisons with experimental values show that the presented calculated values agree with experiment within 0.3 eV (absolute), 0.1 eV (relative).

Results

vic-Diarylethanes (9–11). Recently, the controversy over the bond length in *anti*-**9** has been resolved;^{35,36} the central bond length was established to be consistent with the standard for $C_{sp^3}-C_{sp^3}$ single bonds (1.54 Å). The C_{2h} conformation of diphenylethane thus provides a good reference point for through-bond vs through-space effects. In the C_{2h} anti conformation, the π systems are distant from one another and are unlikely to couple through space, yet the π systems are still well oriented to overlap with the central σ system and couple through bond. Examining the series **9–11**, one should be able to observe changes in through-bond coupling as through-space coupling is enhanced.



The structures and orbitals of **9–11** were evaluated by ab initio Hartree–Fock 6-31G(d) computations. Particular attention was given to the four highest filled orbitals (HOMO through HOMO – 3). These orbitals are formed from various combinations of the single-node degenerate HOMOs of the benzene rings. In each molecule (conformation), one pair of these orbitals contains a node at the $C_{sp^3}-C_{sp^3}$ σ bond and thus can serve as a reference for through-space effects and for the relative energies of the orbitals. The splitting of the other pair of orbitals

reflects a combination of effects, which we consider as the sum of simple through-space and through-bond interactions.

The anti conformation of **9** has orbital energies for HOMO to HOMO – 3 of 8.6, 8.9, 9.0, and 9.0 eV, respectively. The HOMO arises from the $\sigma - S$ combination and is split from the $A + \sigma^*$ combination (HOMO – 1) by 0.3 eV. The two reference orbitals are essentially unsplit (<0.01 eV); this degeneracy is expected due to negligible through-space overlap of the π orbitals separated by more than 4 Å. Thus, through-bond coupling dominates and a bond length of 1.54 Å is observed, less than 0.01 Å different from the standard $C_{sp^3}-C_{sp^3}$ bond length; the bond length in 1,2-dicyclohexylethane (**12**), for which no through-bond coupling is possible, is 1.532 Å (HF/6-31G(D)).

In the syn conformer of **9**, the separation of the π systems is ca. 3 Å and through-space interaction is possible. The HOMO of the syn conformer is the $A + \sigma^*$ combination (8.5 eV) followed closely by the A combination of the reference set (8.7 eV); the virtual degeneracy of these orbitals indicates a minor degree of mixing between A and σ^* . The next orbital is $\sigma - S$ (8.7 eV) followed by the pure S reference (9.0 eV); this difference in orbital energies represents the destabilization of S by mixing with σ . Thus, in the syn conformer, the through-bond splitting (0.3 eV) is equivalent to that found in the anti conformer; however, the through-space splitting increases from 0 to 0.3 eV. The eclipsing interaction in the syn form has lengthened the central bond by 0.03 Å (i.e., 1.57 Å) compared to the anti form, without any change in the amount of through-bond splitting. A similar elongation is seen in eclipsed vs staggered ethane.

Clamping down the back of the rings with a two-carbon bridge, as in **10**, enhances the interaction between the two rings. The HOMO and HOMO – 1 are $A + \sigma^*$ and A combinations (7.8 and 7.9 eV), respectively, indicative of a dominant through-space interaction. The $\sigma - S$ orbital is higher in energy (8.4 eV) than the simple S (9.6 eV). From the difference in orbital splittings between the reference and probe levels, one can deduce a through-bond splitting of ca. 1 eV vs the through-space splitting of ca. 1.7 eV. The central bond of **10** (1.60 Å) is lengthened by another 0.03 Å compared to the syn conformation of **9**. Whether the additional lengthening is due to through-bond coupling can be addressed by examination of a fluorinated derivative of **10**.

Comparison of the PES spectra of **10** and its 1,1,2,2,9,9,10,10-octafluoro analog (**11**) led to the conclusion that fluorination at the sp^3 hybridized carbons of a $\pi-\sigma-\pi$ system “turns-off” through-bond couplings.^{37–40} This conclusion is further supported by the computed orbital energies for HOMO to HOMO – 3 of **11**, $A = A + \sigma^* =$ ca. 9.2 eV, $S = \sigma - S =$ ca. 10.6 eV. The prediction was made that fluorination should lead to shortened C–C bonds in through-bond coupled systems.⁷ An elegantly detailed analysis of the X-ray crystal structures of **10** and **11** was done by Hope, Bernstien, and Trueblood in which they concluded that both compounds had a central bond length of ca. 1.59 Å.⁴¹ In depth study of their analysis reveals that, although the experimental error for these bond lengths is too great to be definitive, if the central bond lengths are not equal between these two derivatives, **10** and **11**, then it is likely that the fluorinated compound possesses the longer bond. Indeed,

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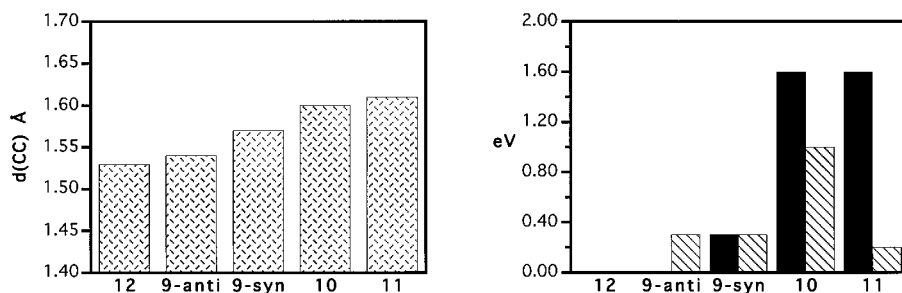


Figure 2. (a, left) Comparison of bond lengths in **9–12**. (b, right) Comparison of through-space (black filled) and through-bond (hatched) couplings in **9–12**.

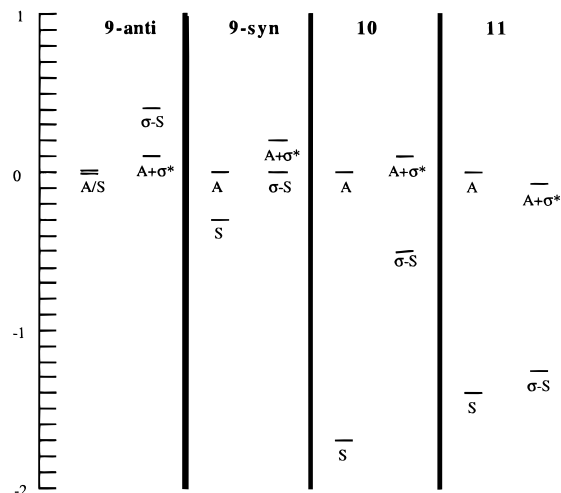


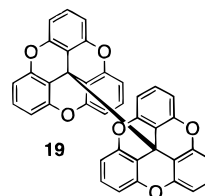
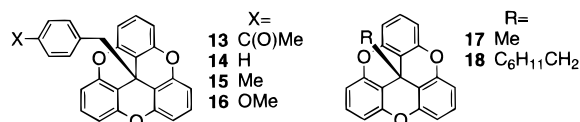
Figure 3. Orbital energies of **9–11** ranked relative to the energy of the A reference orbital.

our HF/6-31G(D) results predict central bond lengths for **10** and **11** of 1.603 and 1.615 Å, respectively. Given that fluorinated alkanes, such as 2,2,3,3-tetrafluorobutane, generally have shorter bonds than their hydrocarbon analogs,^{42,43} this comparison of cyclophane orbital energies and bond lengths directly contradicts the idea that bond lengthening is a function of through-bond coupling (Figure 2).

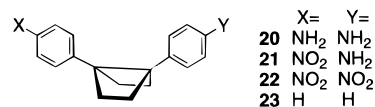
A closer look at the orbital energies across the series **9–11** (Figure 3) shows that the reference A level remains nearly degenerate with the A + σ^* level ($\Delta E =$ ca. 0.1 eV), whereas the $\sigma - S$ level can be significantly higher than the reference S ($0.3 < \Delta E < 1.2$ eV). The approximate equivalence of A and A + σ^* observed throughout this series, and the variable difference between S and $\sigma - S$ is consistent with the view that through-bond coupling in these systems is due primarily to the filled–filled interactions between σ and S, and only negligibly from the filled–empty interaction between A and σ^* . Similar conclusions have been reached from photoelectron spectra^{17–19} and electron transfer^{20–22} studies, and all indicate that bond lengthening of the central bond is not a ramification of through-bond coupling.

Tricornans. The *p*-X-benzyltricornans **13–16** were designed, synthesized, and characterized crystallographically to test the π - σ - π coupling theory in a strain-free but conformationally restricted molecule.^{44,45} As controls, tricornans **17**⁴⁶ and **18**,^{44,45,47} which lack the second π system necessary for

the presence of through-bond coupling in **13–16**, were synthesized and characterized crystallographically. The average central bond length in the X-ray structures of members of the series **13–16** is ca. 1.57 ± 0.01 Å, ca. 0.03 Å longer than the standard C–C single bond. The central bond lengths for **17** and **18** are 1.54 and 1.56 Å, respectively, nearly indistinguishable from the benzyltricornan central bonds. RHF/6-31G(d) calculations of **14** and **18** give central bond lengths of 1.57 and 1.56 Å, respectively; thus, the experimental and computational observations are consistent. In the extreme case of **19**, a hexaphenylethane cognate, a bond length of 1.63 Å is reported.⁴⁸



p,p'-X-diphenyl[2.2.0]bicyclohexanes. In principle, straining the σ system should increase the degree of through-bond coupling without appreciably altering the through-space effect.^{8,9} The *p,p'*-X-diphenyl[2.2.0]bicyclohexanes **20–23** constitute a



classical series for the study of such substituent effects in through-bond coupling; the analogy with diphenylethane is evident. Osawa has concluded in such a study, with the MNDO semiempirical Hamiltonian, that there is significant bond lengthening in diphenyl[2.2.0]bicyclohexane (**23**), and that this bond length is sensitive to substitution, consistent with a through-bond coupled interaction.^{8,11,49} Investigation of the structure of **20–23** by ab initio techniques (RHF/6-31G(D)) reveals that the central and flanking bonds are unaltered, 1.604 ± 0.002 and 1.513 ± 0.002 Å. This distance represents a net 0.002–0.003 Å lengthening over a standard hexasubstituted saturated bond, and is shorter than the computed bond length (1.61 Å) for eclipsed hexamethylethane. In **23**, the through-space splitting of A and S is 0.2 eV, and the splitting of S and $\sigma - S$ is 0.5 eV; A and A + σ^* are essentially degenerate (ΔE

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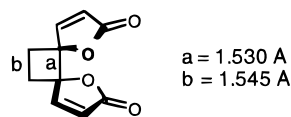
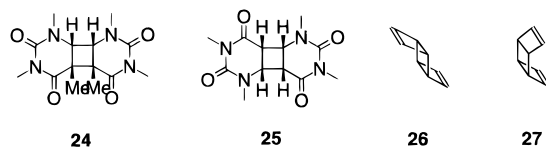


Figure 4. Bridging bond lengths in Anemonin.

< 0.01 eV). Thus, through-bond coupling in these systems is ca. 0.7 eV and dominated by filled–filled interactions, as seen above.

Pyrimidine Dimers and Natural Products. The biochemical importance of pyrimidine dimers such as the dimers of thymidine (**24**) and uracil (**25**) motivated crystallographic investigations of their stereochemistries.⁵⁰ In some key studies, the bonds of the four-membered rings that connected the two pyrimidine units were reported to be unusually long; the longer of the two bridging bonds in the four-membered ring is the less sterically hindered one, 1.66 vs 1.60 Å. Dougherty et al. concluded, “This bond-lengthening may be taken as *prima facie* evidence for through-bond interactions between the N-C(O)-N-C(O) π systems.” and claimed that, “Although cyclobutane bonds naturally tend to be longer ... the magnitude of the bond-lengthening, particularly in [**24**], is such that factors other than mere steric effects are likely to be operative.”⁷ Given such unusual experimental parameters, strong theoretical claims, and our own inability to find any evidence for bond-lengthening from through-bond coupling, we felt it necessary to revisit these structures.



As noted above, it was stereochemistry and not specific internal geometry that motivated the crystallographic studies of **24** and **25**. A cursory glance at the actual experimental details for **24** reveals that the quality of the internal coordinate data is lacking. The original authors were themselves wary of the geometrical reliability of their data. They clearly disclaimed “Because of the impossibility of obtaining high-accuracy intensity data due to the monomerization of the dimers by X-rays, the standard deviation of the bond lengths and angles are rather high: 0.025–0.035 Å.”⁵⁰ At an uncertainty of 3σ , this deviation places error bars on the bond lengths of ca. ± 0.1 Å. Ab initio calculations (RHF/6-31G(d)) of the structure of **24** predict bridging bond lengths of 1.595 and 1.559 Å, with the longer bond bridging the sterically more hindered atoms. This reasonable structure discounts the notion of through-bond coupling as the mechanism for bond lengthening in the thymidine dimer and points to obvious experimental error. Similar computations of **25** corroborate these results and predict bridging bond lengths of 1.55 and 1.57 Å.

In another series of strained compounds (**26**, **27**), Gleiter and Heilbronner gauged the through-bond coupling to be around 1 eV, with a through-space interaction of 0.4 eV in **27**.⁵¹ Our HF/6-31G(D) results predict bond lengths of 1.553 and 1.578 Å for **26** and **27**, respectively. Thus, strong through-bond coupling does not seem to lengthen even these strained bonds.

Another dimer, with the possibility of manifesting bond lengthening from through-bond effects, is present in the alkaline extract of the buttercup and other ranunculaceae. The structure of this natural product, Anemonin (Figure 4), was investigated

by Moriarty and Karle in 1965,⁵² before the proposal of bond lengthening by through-bond coupling. In their analysis of the structure they conclude “The C–C bond lengths in the cyclobutane ring range from 1.530 Å to 1.545 Å, a normal range for single bonds.”

***p*-Dibenzene and the Anthracene Dimers.** In the series **4–8**, the π systems are held in position to conjugate with the central σ bond, the central σ bonds are strained, and the symmetry of the system allows for multiple interactions. As such these systems should provide the signal examples of bond lengthening from through-bond coupling. Indeed, the originally reported structure of **6** contains a spectacular (and often cited) 1.77 Å central C–C single bond;⁵³ however, our redetermination of this structure at 170 K shows the true length as a far less unusual 1.648 Å.¹³ The X-ray structure of **8** at ambient temperature or at 150 K features a central bond length of 1.64 Å.^{13,54} Though less spectacular than originally thought, these single bonds are long and deserve further comment and investigation.

Hartree–Fock (HF) and density functional theory (DFT) computations on **4–8** agree well with experiment, and demonstrate a significant bond lengthening of ca. 0.1 Å compared to standard C_{sp^3} – C_{sp^3} bonds though not outside the realm of what has been seen in heavily sterically encumbered systems.^{55,56} Given the exceptional strain in the σ -frame of these compounds and the potential aromatic stabilization of the dissociated products, one might believe that this class of structures could show special effects not seen elsewhere; however, analysis of the orbital energies of **4–8** presents a familiar picture in which through-space interactions have strong effects on A and S combinations but that through-bond effects are primarily arising from the raising of $\sigma - S$. Although these orbital effects are hard to factor out of a single complex compound, a series analysis of related compounds is illuminating. Computations on **4**, its three tetrahydro (gem, syn, anti) and one hexahydro derivatives provided data on 11 molecular orbitals where through-bond (TB), hyperconjugation (HC), or through-space (TS) effects could occur. Single-point computation of ethylene constrained to the fragment geometry of a double bond in **4** provides the base π orbital energy. From these systems a series of 12 equations (one for each orbital) and 7 unknowns (one for each effect plus the base value) can be formulated. Matrix regression on this overdetermined set of linear equations gives the following “best fit” factor analysis: base value = 9.98 eV; HC(σ) = 0.78 eV; HC to σ^* = 0.08 eV; TB($\sigma - S$) = 1.231 eV; TB(A + σ^*) = 0.12 eV; TS(gem) = 0.88 eV; TS(syn) = 0.80 eV. From these factors any orbital energy in the series can be reconstructed within a value of 0.2 eV. The qualitative aspects of this analysis suggest that no special orbital coupling effects are at play in **4** and cognates. The quantitative aspects of the analysis indicate that TB(A + σ^*) and HC (σ^*) effects are negligible! Computations were also performed on the 1,1',6,6'-tetrafluoro derivative of **4** to study the fluorine effect of reducing through-bond coupling. The only orbital that significantly changed relative energy was the $\sigma - S$, which dropped in energy indicative of a reduced interaction; the A + σ^* was essentially unchanged. In addition, the 1,1' bond length did not shorten, further evidence that through-bond coupling was not an important structure-determining factor in the parent.

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Thus, it is our assertion that, even for **4**–**8**, steric/electrostatic⁵⁷ repulsion not through-bond coupling is the dominant cause of bond elongation. A classical steric argument should not be surprising, as the proximal atoms of the π systems lie only 2.8 Å apart, well within the sum of van der Waals (vdW) radii (3.6 Å).⁵⁸ Additional repulsion between the face to face arenes may come from the polar nature of the π cloud.^{59–62}

One reviewer has conjectured that CH₂ is in all cases sterically more demanding than CH and therefore asserted that sterics cannot account for the bond lengthening in **4** vis-à-vis **4a** ergo the effect must arise from through-bond coupling. Two final points on this: One, his original conjecture is not true as can be seen in the steric cyclohexane A values of phenyl and cyclohexyl. Although the situation for cyclohexane and the present study are not identical, who is to say we know for sure how we should rank the steric effect of CH₂ vs CH in this environment? Two, summation of the lengthening effects seen in *gem*-**4**, *syn*-**4**, and *anti*-**4** predicts the structure of **4** well with *gem*-**4** and *syn*-**4** effects dominating the equation. Thus, no new effects need be considered and in the case of *trans*-**4**, where exclusively through-bond coupling should be acting, there is essentially no change in bond length.

SE vs EFF: Comparisons and Dissections. One outcome of the early π - σ - π through-bond coupling discussion was the belief that one can detect bond lengthening due to through-bond coupling simply by comparing EFF and SE calculations of a molecular structure, because EFF calculations lack a “through-bond” term. For example, Dougherty et al.⁷ state, “Our preliminary study on a comparison of bond lengths calculated by EFF with the experimental values and calculations of CNDO overlap populations...” and the “...significantly longer bond calculated by [the SE method] MINDO/3 can be taken as direct evidence for a bond lengthening which is not included in the EFF.” Osawa and Kanematsu⁹ similarly claim, “Comparison of MO and MM results turned out to be a convenient way of detecting the bond elongation by the through-bond mechanism.” Indeed, as discussed above, calculated bond length differences such as these have been a major argument for the existence of bond lengthening from through-bond coupling in π - σ - π systems.^{6–12,63}

From what is known about the variability in EFF and SE calculations, it is clear that relying on such semiempirical data as a surrogate experimental reference for EFF comparisons is untenable. Indeed, it is common for structural predictions and specific lengths as well as relative conformational energies to vary widely with the choice of semiempirical Hamiltonian (for example in the case of **13**–**16**).^{44,45,64} In this series, the data are so varied that, in the absence of experiment, comparison of EFF with semiempirical (AM1) results gives the impression that the fit is quite good, whereas comparison of EFF with semiempirical (MNDO) results betrays a large difference in the

predicted bond lengths. With such variable data, many theoretical “effects” could be justified by judicious choice of Hamiltonian even if no “effects” were actually significant.

Furthermore, even though additional EFF parameters might improve the structural fit for compounds discussed herein, assigning specific physical significance to any partitioned parameter is arbitrary.⁶⁵ It has been long recognized that partitioning the strain energies of an EFF calculation has no physical significance because of the dependence on the reference set of compounds used for regression and the particular weighting of different terms in the force field.⁶⁵ The EFF will, to the best fit possible, mimic all features of the reference set of compounds, and the form of the terms will determine the weighting within the regression analysis. Thus, two force fields with different reference compounds and different terms can still each well predict a given structure and its total strain energy, but display widely different partitioning of energy terms. The semiempirical Hamiltonians also have empirical parameters associated with them.

In short, there are two points here: (1) it is inappropriate to use quantum computations or even experimental results in comparison with EFF computations to extract “nonsteric” effects; (2) it is inappropriate to attribute partitioned EFF energies to through-bond coupling effects. We mention these semiempirical/EFF studies because of their pervasive character throughout through-bond discussions, but we categorically disagree with their use as regards bond lengthening in through-bond coupled systems, and we feel it erroneous for additional EFF terms to be considered as through-bond coupling or hyperconjugation terms.^{66,67}

Conclusion

The classical ideas of through-bond and through-space orbital coupling are useful for explaining the calculated orbital energies and experimental photoelectron spectra of a variety of polyarylethanes. Through-bond coupling is a result primarily of the filled-filled interaction between the symmetric combination of π orbitals with the σ bonding orbital; little to no mixing occurs between the antisymmetric π combination and σ^* . Through-bond coupling is a net destabilizing interaction which raises the average π orbital energy. The magnitude of the through-bond coupling does not correlate with the central bond length. Previous conclusions that through-bond coupling induces long bonds relied in some cases on poor X-ray data and/or inappropriate molecular orbital theories to deduce geometries. Redetermination of these geometries by improved experiments and higher level computational methods indicates that bond lengthening by through-bond coupling is not significant (i.e., never has more than a 2–3 pm effect and usually is less than 1 pm). Comparison of semiempirical and empirical force field data as a geometrical test for through-bond coupling is unwarranted. Addition of a “through-bond coupling” term to existing force fields may improve the regression fit but does not reflect

(57) It is clear that there is still much for us to learn about the face to face interactions of aromatics.^{59–62} Recently, Leutweiler has found that the “normal” vdW surface for arenes should be extended in the direction perpendicular to the plane of the ring: Leutweiler, S. Private communication. Irngartinger has also studied the anisotropic distribution of electron density in π systems; see: Irngartinger, H. *Electron Distribution in the Chemical Bond*; Plenum Press: New York, 1982.

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(65) “By itself E has no physical meaning. In addition, the component terms ... will change depending on their functional forms and choice of parameters.” (p 269); “Thus, the values of individual terms, such as stretching, or torsion, etc., have no absolute meaning.” (p 273) Boyd, D. B.; Lipkowitz, K. B. *J. Chem. Educ.* **1982**, *59*, 269–274.

(66) Allinger and Katzenellenbogen have found that inclusion of a new term in the MM3 force field allows them to pick up subtle variations in benzylic bond lengths. The improvement in fit is clear, although proof of hyperconjugation as the mechanism remains in our minds unsubstantiated; see: Allinger, N. L.; Chen, K.; Katzenellenbogen, J. A.; Wilson, S. R.; Anstead, G. M. *J. Comput. Chem.* **1996**, *17*, 747.

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a physically significant measure of through-bond coupling. Although the present full structural analysis reduces the significance of classical π - σ - π conjugation arguments with regard to bond lengthening, this does not mean that there are not special cases where such arguments are important. At the state of bond cleavage, stabilizing filled/empty π - σ - π effects are significant;⁶⁸ thus, for molecules like bullvalene or radical cations/anions, significant geometrical effects due to π - σ - π through-bond coupling are more likely.

Appendix

Computations on **4**, its three tetrahydro- (gem, syn, anti), and one hexahydro- derivatives provided data on 11 molecular orbitals where through-bond (TB), hyperconjugation (HC), or through-space (TS) effects could occur. Single-point computation of ethylene constrained to the fragment geometry of a double bond in **4** provides the base pi-orbital energy (BV). From these systems, a series of 12 equations (one for each orbital) and 7 unknowns (one for each effect plus the base value) can be formulated as follows:

model alkene = BV				= -10.3
4 -a	= BV + 1.0HC σ - 1.0HC σ^*			= -9.15
4 -gem, S	= BV + 1.4HC σ - 1.4HC σ^* - 1.0TS $_g$			= -9.38
4 -gem, A	= BV	+ 1.0TS $_g$		= -8.92
4 -syn, S	= BV		- 1.0TS $_{syn}$ + 1.0TB σ	= -9.35
4 -syn, A	= BV		+ 1.0TS $_{syn}$ - 1.0TB σ^*	= -8.77
4 -anti, S	= BV		+ 1.0TB σ	= -8.70
4 -anti, A	= BV		- 1.0TB σ^*	= -9.90
4 , SS	= BV + 2.0HC σ		- 1.4TS $_g$ - 1.4TS $_{syn}$ + 1.4TB σ	= -9.24
4 , SA	= BV	- 2.0HC σ^* - 1.4TS $_g$ + 1.4TS $_{syn}$		- 1.4TB σ^* = -9.94
4 , AS	= BV	+ 1.4TS $_g$ - 1.4TS $_{syn}$		= -9.98
4 , AA	= BV	+ 1.4TS $_g$ + 1.4TS $_{syn}$		= -7.79

Solving this system of equations for the vector $\mathbf{x} = (BV, HC_\sigma, HC_{\sigma^*}, TS_g, TS_{syn}, TB_\sigma, TB_{\sigma^*})$ involves solving $\mathbf{Ax} = \mathbf{b}$, where

$$\mathbf{A} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & -1 & 0 & 0 & 0 & 0 \\ 1 & 1.4 & -1.4 & -1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & -1 & 1 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 & -1 \\ 1 & 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & -1 \\ 1 & 2 & 0 & -1.4 & 1.4 & 1.4 & 0 \\ 1 & 0 & -2 & -1.4 & 1.4 & 0 & -1.4 \\ 1 & 0 & 0 & 1.4 & -1.4 & 0 & 0 \\ 1 & 0 & 0 & 1.4 & 1.4 & 0 & 0 \end{pmatrix} \quad \mathbf{b} = \begin{pmatrix} -10.3 \\ -9.15 \\ -9.38 \\ -8.92 \\ -9.35 \\ -8.77 \\ -8.70 \\ -9.90 \\ -9.24 \\ -9.94 \\ -9.98 \\ -7.79 \end{pmatrix}$$

such that

$$\begin{aligned} \mathbf{Ax} &= \mathbf{b} \\ \mathbf{A}^T \mathbf{Ax} &= \mathbf{A}^T \mathbf{b} \\ [\mathbf{A}^T \mathbf{A}]^{-1} \mathbf{A}^T \mathbf{Ax} &= [\mathbf{A}^T \mathbf{A}]^{-1} \mathbf{A}^T \mathbf{b} \\ \mathbf{x} &= [\mathbf{A}^T \mathbf{A}]^{-1} \mathbf{A}^T \mathbf{b} \end{aligned}$$

This analysis then gives

$$\mathbf{x} = \begin{pmatrix} -9.98 \\ 0.78 \\ -0.08 \\ 0.88 \\ 0.80 \\ 1.23 \\ -0.12 \end{pmatrix}$$

or BV = 9.98 eV, HC(s) = 0.78 eV, HC(σ^*) = 0.08 eV, TB(σ - S) = 1.23 eV; TB(A + σ^*) = 0.12 eV, TS(gem) = 0.88 eV; and TS(syn) = 0.80 eV. From these factors, the orbital energies in the series can be reconstructed as

$$\mathbf{OE}_{\text{calc}} = \begin{pmatrix} -9.98 \\ -9.12 \\ -9.66 \\ -9.10 \\ -9.55 \\ -9.06 \\ -8.75 \\ -9.86 \\ -9.06 \\ -9.76 \\ -9.87 \\ -7.62 \end{pmatrix}$$

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