Pure Appl. Chem., Vol. 85, No. 5, pp. 921–940, 2013.
http://dx.doi.org/10.1351/PAC-CON-13-01-03

Hyperconjugation in hydrocarbons: Not just a "mild sort of conjugation"*

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Abstract: This article emphasizes two underappreciated aspects of hyperconjugation in hydrocarbons, two-way hyperconjugation and hyperconjugation in tight spaces. Nonplanar polyenes [e.g., cyclooctatetraene (D_{2d}), biphenyl (D_2), styrene (C_1)], the nonplanar rotational transition states (TSs) of planar polyenes (e.g., perpendicular 1,3-butadiene), as well as the larger nonplanar Hückel or Möbius annulenes, are stabilized by effective σ-electron delocalization (involving either the C–C or C–H bonds) via *two-way hyperconjugation*. The collective consequence of two-way hyperconjugation in molecules can be nearly as stabilizing as π-conjugation effects in planar polyenes. Reexamination of the σ- vs. π-bond strength of ethylene results in surprising counterintuitive insights. Strained rings and cages (e.g., cyclopropane and tetrahedrane derivatives, the cubyl cation, etc.) can foster unexpectedly large hyperconjugation stabilizations due to their highly deformed ring angles. The thermochemical stabilities of these species rely on a fine balance between their opposing destabilizing geometrical features and stabilizing *hyperconjugative effects in tight spaces* (adjustable via substituent effects). We hope to help dispel chemists' prejudice in viewing hyperconjugation as merely a "mild" effect with unimportant consequences for interpreting the structures and energies of molecules.

Keywords: carbocations; cyclopropane; electron delocalization; hyperconjugation; nonplanar polyenes; twisted ethylene.

INTRODUCTION

Chemists typically consider π- rather than σ-effects as having far more impact on the chemical behavior of molecules. This emphasis is justified by frontier orbital considerations. The connectivity between atoms (the "skeleton" of the molecule) is usually determined by lower-lying σ-bonding orbitals, but it is the higher-lying frontier orbitals (which often have π-symmetry) that direct the chemistry of molecules. Many π-type effects, π–π stacking, aromaticity, conjugation, etc. are very useful to derive highly transferable chemical principles that shape our chemical intuition. Such concepts help the understanding, interpretation, and prediction of the structure–energy relationships of diverse types of molecules. However, we show here that σ-framework effects (e.g., hyperconjugation considered here) can have important, highly enlightening chemical consequences. Mulliken's 1939 description of hyperconjugation as "a mild sort of conjugation" [1] has been perpetuated as the standard view. But this perception needs reconsideration from today's viewpoint. We review several examples in hydrocarbons where this is not true. Chemists tend to underestimate the magnitude of hyperconjugation effects, since evaluations

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Pure Appl. Chem.* **85, 883–956 (2013). A collection of invited, peer-reviewed articles by the winners of the 2012 IUPAC Prize for Young Chemists.

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often are based on *differences* rather than *direct estimates* of hyperconjugative stabilization. Interpretations of the origin of the rotational barrier of ethane afford an excellent example. Whatever its origins may be, the 3 kcal/mol barrier is *not* a measure of the maximum possible hyperconjugation effect, but only the difference in hyperconjugation between the eclipsed and staggered forms. Thus, computed absolute estimates of the hyperconjugative stabilization in staggered and eclipsed ethane are both quite large (on the order of 10–11 kcal/mol). In this article, we use the term "hyperconjugation" broadly to describe stabilizing σ-electron delocalization effects, e.g., from a σ-bond to an adjacent empty or partially filled π*-orbital, or to a geminally or vicinally positioned σ*-bond orbital. Hyperconjugative effects, even when only σ-bond orbitals are involved, can be quite substantial (as in ethane, above) in the following circumstances: (1) when many interactions are present in a molecule and thus can accumulate to an overall large stabilizing effect, or (2) when the hyperconjugating orbitals are confined to close proximity in molecules with very compact geometries, i.e., in *tight spaces* [3]. This article presents a collection of our personal views and interpretations of such examples in light of the prior literature and our new computational findings. Readers interested in an excellent broader overview of hyperconjugation are encouraged to consult Alabugin et al.'s recent comprehensive review [4].

TWO-WAY HYPERCONJUGATION

Half a decade before he invented the term "hyperconjugation", [1] Mulliken noted, "a 90º rotation of the two parts of a C_2H_4 molecule after all does not entirely destroy the second bond of the double bond" [1c]. Disrupting the π-bond by rotation does not fully eliminate π-stabilization in ethylene! Instead, the rotational transition state (TS) of ethylene is stabilized by hyperconjugation between the CH and π-orbitals on opposite ends of the rotated C–C bond (see Fig. 1a). This stabilization compensates for part of the loss of a π-bond and lowers the rotational barrier of ethylene.

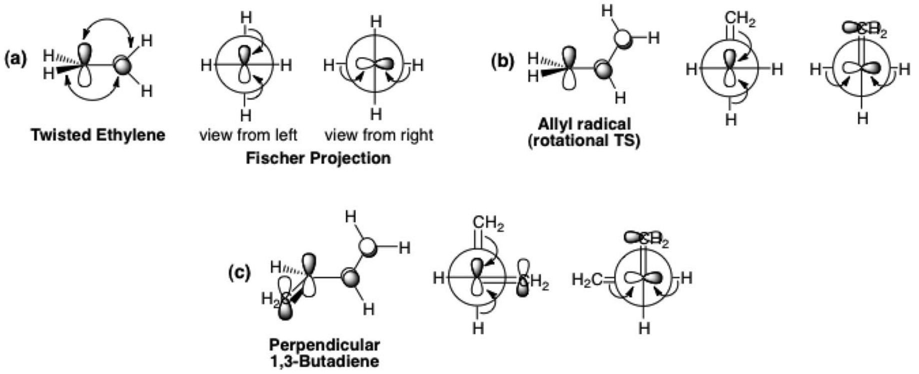

Fig. 1 Schematic illustration of two-way hyperconjugation in (a) twisted ethylene (C–H → π* and π → C–H*); (b) allyl radical (σ-CH → π*, σ-CC → π*, π → σ-CH*, and π → σ-CC*); and (c) *perp*-butadiene (σ-CH → π*, σ-CC → π*, π → σ-CH*, and π → σ-CC*).

For this reason, the triplet ethylene minimum adopts a D_{2d} ground state 16.9 kcal/mol lower in energy than its nearly planar (C_{2v}) rotational TS [5] (see Fig. 2a). The D_{2d} minimum of the ethylene dication ($C_2H_4^{2+}$) and diboryl (B_2H_4) also are 28.1 kcal/mol [6] and 10.9 kcal/mol [7] lower in energy than their D_{2h} TSs. Ironically, the most common (but incorrect) textbook evaluation of the π-bond strength of ethylene (65.8 kcal/mol, see Fig. 2b [5]) is based on the energy required to twist one of the CH_2 groups by 90º [8–10]. But this overlooks Mulliken's proposition, and "assumes that the rotational TS of ethylene has no π-bond character" [8]. Conventional estimates of the π-conjugation energies, e.g., of the allyl radical (15.7 kcal/mol) [11], 1,3-butadiene (5.9 kcal/mol, anti-gauche barrier) [12], and

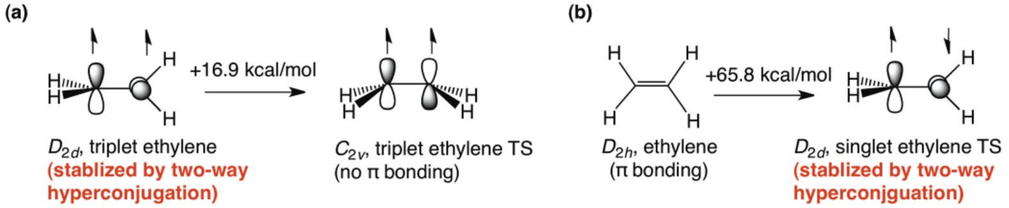

Fig. 2 Two-way hyperconjugation in the (a) D_{2d} triplet ethylene minimum and (b) singlet ethylene rotational TS.

other planar polyenes, based on their rotational barriers suffer from the same problem (see Figs. 1b and 1c). Perpendicular (*perp-*) butadiene is not devoid of π-stabilization either, but benefits from hyperconjugation, back-and-forth (i.e. "two-way") between the C–H/C–C bonds and their adjacent π-orbitals, across the twisted central C–C bond (see Fig. 1). In view of the broad applicability of such effects, Wu, Fernández, Mo, and Schleyer coined the term *two-way hyperconjugation* to describe the hyperconjugation stabilization of polyenes (or their rotational TSs) with nonplanar equilibrium geometries [13]. This section discusses key cases of two-way hyperconjugation and how its realization changes our interpretation of even the simplest and most well understood organic molecules (e.g., ethylene, 1,3-butadiene, cyclooctatetraene, etc).

Importantly, two-way hyperconjugation is not a small effect, but can provide rather large stabilizations, especially when many such interactions are present in a molecule. Based on primitive self-consistent field (SCF) computations, Daudey et al. reported that π-conjugation in planar *anti*-butadiene (10.4 kcal/mol) and hyperconjugation in the *perp*-butadiene (8.9 kcal/mol) were of "the same order of magnitude," and that both effects led to "a similar shortening of the central bond" (ca. 0.045 Å for *anti*-butadiene, ca. 0.042 Å for *perp*-butadiene) [14]. Mulliken recognized that hyperconjugation compensated for some of the lost π-electron delocalization in *perp*-butadiene much earlier, but estimated a much lower value (3.2 kcal/mol) [15]. Didactically, *perp*-butadiene is often presented as a polyolefin model devoid of π-stabilization. On this basis, George et al. suggested the use of *perp*-butadiene as a reference compound for evaluating the stabilization energies of conjugated hydrocarbons [16]. Fellar et al. proposed that the central C–C bond of *perp*-butadiene (1.482 Å) modeled a pure C_{sp2}–C_{sp2} bond length [17]. However, Wu and Schleyer et al.'s natural bond orbital (NBO) analysis of 1,3-butadiene disputes such erroneous usage. They demonstrated definitively that deviation of the CCCC dihedral angle of 1,3-butadiene from planarity reduces π-conjugation gradually (see Fig. 3, solid line), but this is replaced by increasing two-way hyperconjugation, which reaches a maximum at a 90° CCCC dihedral angle (see Fig. 3, dashed line) [13].

Although the individual hyperconjugative interactions (see Fig. 2b) in *perp*-butadiene are less stabilizing compared to π-conjugation in the planar (*syn-* or *anti-*) forms, the variety of hyperconjugative interactions present in *perp*-butadiene can accumulate to give quite substantial overall stabilizing effects. Notably, not only CH bonds, but also CC σ-bonds hyperconjugate [18,19] (however, Alabugin et al.'s review on this subject points out that, "the relative ability of many common σ-donors, including the most ubiquitous case of C–H versus C–C, still is widely debated" [see discussion in ref. 4 and literature cited therein]). Hence, all the various conformers of butadiene are stabilized, by conjugation (0° and 180° conformers), hyperconjugation (the 90° conformer), or a blend of the two effects (i.e., the intermediate 0°–90° and 90°–180° conformers) (see Fig. 3). This conjugation vs. hyperconjugation interplay rationalizes the low experimental *anti* → *gauche* butadiene single C–C bond rotational barrier (5.9 kcal/mol) [12]; unexpected in view of the 14.3 kcal/mol π-conjugation of *anti*-butadiene (estimated by the bond separation equation: 1,3-butadiene + 2 methane → 2 ethylene + ethane [20], based on experimental heats of formation). Rotational barriers do not provide satisfactory estimates of the π-energies of polyenes, since the nonplanar TSs also are stabilized [1,15,21].

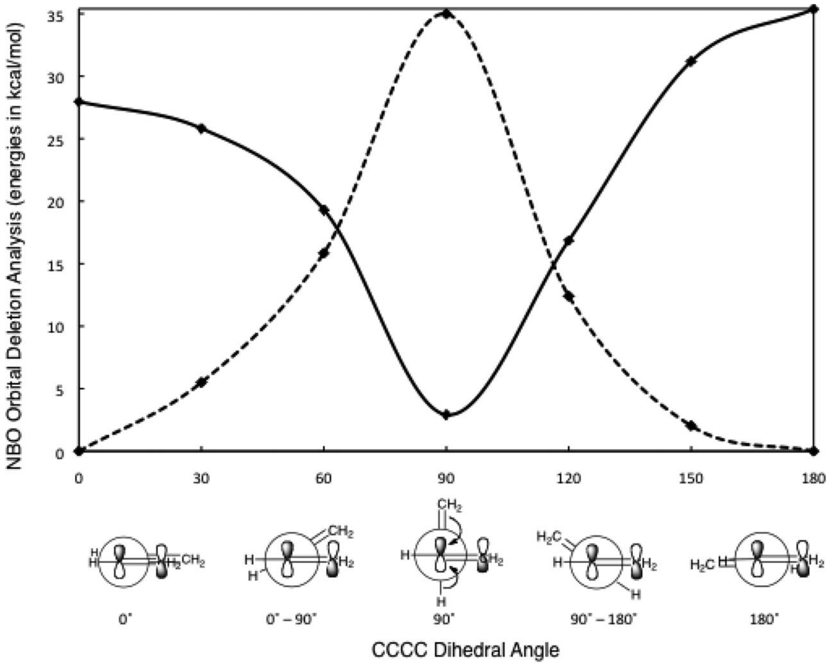

Fig. 3 Conjugation (solid line) and hyperconjugation (dashed line) interconversion upon the central C–C bond rotation of 1,3-butadiene (CCCC dihedral angle rotated at 30º intervals), estimated by computed NBO second-order perturbation analysis (at HF/6-31G*) (adapted from ref. [13]).

For the same reason, the nonplanar geometries of biphenyl (D_2, 44.4º torsional angle) [22] and styrene (C_1, 27.2º torsional angle) [23] benefit from partial π-conjugation and two-way hyperconjugation. Likewise, Pitzer noted early that, "another complication [regarding the rotational barrier of styrene] is the hyperconjugation or second order conjugation still present when the vinyl group is perpendicular to the phenyl group" (see Fig. 4a) [21]. Based on vertical block-localized wavefunction (BLW) computations [24], Wu and Schleyer estimated the *inter-ring* π-conjugation stabilization of the *planar*-biphenyl TS (9.1 kcal/mol) and two-way hyperconjugation in the *perp*-biphenyl TS (7.5 kcal/mol) (i.e., interactions between the two phenyl rings) to be quite similar (B3LYP/6-31+G*) [13]. For this reason, the $D_2 \rightarrow D_{2h}$ (planar, 1.6 kcal/mol, expt.) and $D_2 \rightarrow D_{2d}$ (perpendicular, 1.4 kcal/mol, expt.) rotational barriers of biphenyl [22] are both extremely low and nearly equal. The inclusion of highly polarizable heteroatoms (e.g., sulfur) when placed strategically [25], promote even more effective π-conjugation and two-way hyperconjugation in similar systems. According to the same BLW procedure, the inter-ring π-conjugation between the two thiophene rings in planar 2,2-bithiophene (16.0 kcal/mol) and two-way hyperconjugation (CS → π* and π → CS*) in the perpendicular form (14.3 kcal/mol, see Fig. 4b) are both nearly *twice* that of biphenyl (at B3LYP/6-31+G*). Like biphenyl, the nonplanar *trans*-2,2-bithiophene (146º SCCS torsional angle) also has low rotational barriers via its planar (0.4 kcal/mol) and perpendicular (1.8 kcal/mol) TSs. By the same token, the computed ACID (anisotropy of the induced current density, see Fig. 4c [26]) plots of the *planar*- and *perp*-bithiophene TSs have similar critical isosurface values (CIVs) (planar: 0.077, perpendicular: 0.080 [27]) and both display continuous delocalized electron density between the two thiophene rings. The ACID isosurface reflects the density of mobile electrons in a molecule and is useful for visualizing ring currents and electron delocalization [26].

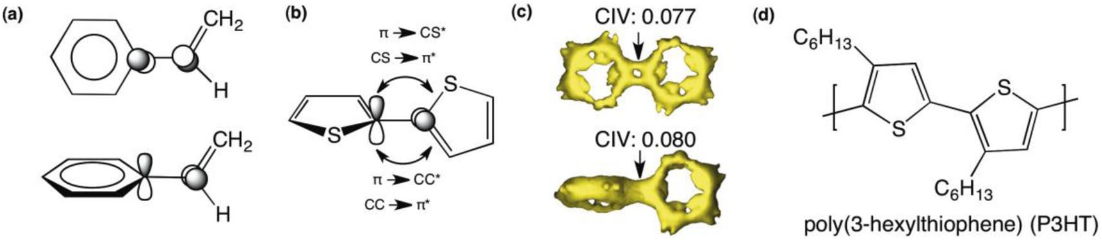

Fig. 4 (a) *Planar-* and *perp*-styrene TSs; (b) two-way hyperconjugation in *perp*-bithiophene; (c) computed ACID plots and CIVs for *perp-* and *planar*-2,2-bithiophene [27]; (d) P3HT.

The torsional profiles of oligothiophenes (and presumably other oligomers and polymers) involve a similar conjugation vs. hyperconjugation interplay. The consequences have not been considered explicitly in the literature. However, Darling reported that poly(3-hexylthiophene) (P3HT) (see Fig. 4d) chains involving a single inter-ring SCCS dihedral angle does not extinguish charge transfer, even at an extreme 90º dihedral angle [28]. This challenged the common belief that torsional defects (i.e., large inter-ring dihedral angles) in oligomers preclude π-conjugation and inhibit charge mobility. The explanation offered here is the involvement of two-way hyperconjugation, which is operative at the twisted bithiophene junctions.

Despite being the standard unconjugated polyene model used in many organic textbooks, the tub-shaped cyclooctatetraene minimum (D_{2d}, 56º CCCC dihedral angles) is far from being conjugation free. Actually, the isodesmic bond separation stabilization energy of D_{2d} cyclooctatetraene (41.1 ± 1.5 kcal/mol) [29] is only modestly less than that of the fully conjugated aromatic benzene (64.6 ± 1.1 kcal/mol) [13] (see Fig. 5a)! The CC bond lengths of cyclooctatetraene also are peculiar. Fellar et al. noted, “the C=C bond(s) (1.337 Å) seem too long, and the C–C bond(s) (1.470 Å) too short,” for being effectively unconjugated, and thus “some π electron delocalization” must occur [17]. These energetic and geometric features underscore Mulliken’s 1959 comment that “twisting of two adjacent double

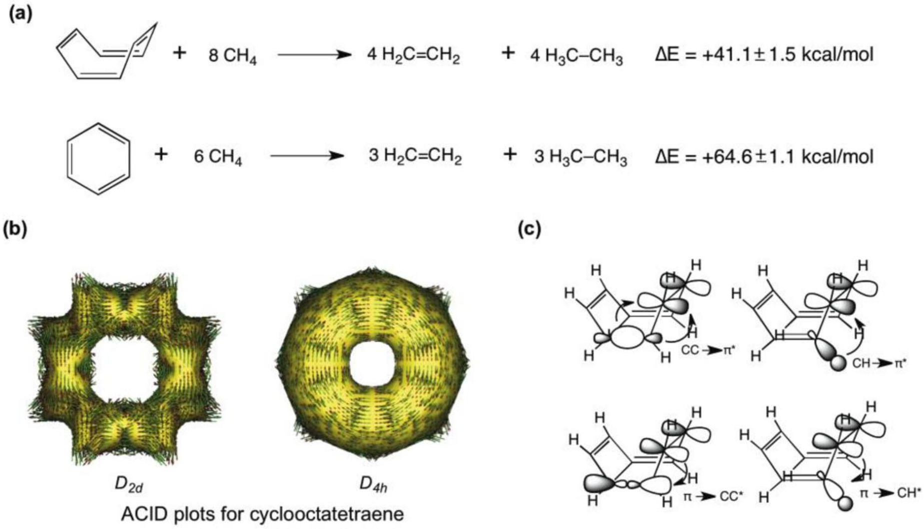

Fig. 5 (a) Isodesmic bond separation equation for cyclooctatetraene and benzene, evaluated based on experimental heats of formation; (b) ACID plots for D_{2d} and D_{4h} cyclooctatetraene [27]; (c) hyperconjugation back-and-forth across the twisted C–C bonds of the D_{2d} cyclooctatetraene minimum (adapted from ref. [8]).

bonds so that their planes become perpendicular (as is approximately true in cyclooctatetraene)" "creates a first-order hyperconjugation at both ends of the C–C bond" "thus, some resonance shortening is expected" [15]. Wu and Schleyer demonstrated by BLW computations that electron delocalization among the four HC=CH units actually stabilized both the D_{2d} (56.9 kcal/mol) and D_{4h} (57.7 kcal/mol) forms of cyclooctatetraene to nearly the same extent [13]. There is substantial electron delocalization in the tub-shaped cyclooctatetraene minimum! Computed ACID isosurfaces also show considerable delocalized electron density (see Fig. 5b) for both D_{2d} and D_{4h} cyclooctatetraene, even though the former lacks any visible "ring current" (see Fig. 5b) [30]. Although planar D_{4h} cyclooctatetraene is stabilized by four $\pi \rightarrow \pi^*$ conjugations (despite its putative antiaromaticity), D_{2d} cyclooctatetraene is stabilized by blends of residual π-conjugation and eight pairs of two-way hyperconjugation (CC → π*, CH → π*, π → CH*, and π → CC* interactions, back-and-forth across the twisted C–C single bonds, see Fig. 5c). These hyperconjugative interactions compensate for the substantial, but not complete, loss of π-conjugation upon ring puckering.

Möbius (and nonplanar Hückel) annulenes also are subject to some if not substantial two-way hyperconjugative stabilization, as indicated from the distinct features of these highly twisted rings. Möbius rings are characterized by an odd number of electronic half-twists and follow a modified Hückel rule for aromaticity [31]. Möbius 4*n* π-electron rings are expected to show aromatic character, while 4*n* + 2 π-electron rings are antiaromatic. Since twisting would inevitably lead to higher ring strain and reduced p_π-orbital overlap in Möbius rings, Heilbronner proposed that only very large rings (>20 ring atoms) would be viable [32]. He assumed that the nonplanar geometries of 4*n* π-Möbius cycles should suffer no loss of π-conjugation provided that the "twist" is evenly distributed around the ring to allow a more or less continuous array of π-overlap [33] (but it is impossible to draw a *continuous* Möbius strip using only signed p_π-orbitals, see Fig. 6a and text below). But many theoretical examples disprove such requirements. Several computationally identified aromatic 4*n* Möbius candidates, e.g., $C_9H_9^+$ [33], $C_{13}H_{13}^+$ [34], $C_{14}H_{14}^{2+}$ [35], and the Möbius [12] and [16]annulenes [36], have less than 20 ring atoms and large torsional angles (40–70° deviation from maximum p_π–p_π overlap), but are thermochemically competitive (or even more stable [33,34]) compared to their Hückel isomers. The aromatic character of these Möbius rings (necessarily sustained by a cyclic electron delocalization, see, e.g., Fig. 6b, $C_{14}H_{14}^{2+}$) anticipates the involvement of two-way hyperconjugation at junctions with large CCCC dihedral angles that deviate from planarity. Note that the common depictions of Möbius systems, introducing a 180° phase shift in an array of p_π, essentially "breaks" π-overlap, is inaccurate, and does not follow Heilbronner's idea (see Fig. 6a). A *continuous* Möbius strip can be achieved only through σ–π mixing (the rehybridization of s- and "non-π" p-orbitals, i.e., orbitals that do not have a nodal surface through the carbon skeleton of the molecule), and anticipates the involvement of hyperconjugation. Wannere et al. pointed out, "if the σ-π mixing perturbation is disregarded, no single canonical molecular orbital can have Möbius character" [37].

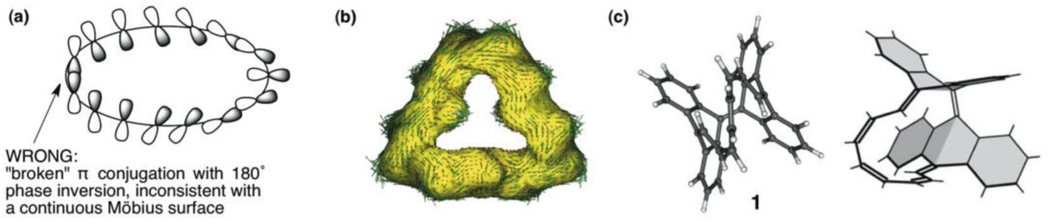

Fig. 6 (a) The common inaccurate depiction of Möbius strips with an array of p_π-orbitals; (b) ACID plot (adapted from ref. [35]) for Möbius $C_{14}H_{14}^{2+}$; (c) Ajami et al.'s [16]annulenic Möbius compound **1** (adapted from ref. [38b]).

In 2003, Ajami et al. announced the synthesis of the first crystalline möbius hydrocarbon (**1**, see Fig. 6c) [38a,b] featuring a 16π-electron bianthroquinodimethane pathway. Despite the well-earned attention to this achievement, **1** elicited much debate concerning its aromaticity. Castro et al. commented that the [16]annulene pathway of **1** contained several torsional angles that deviated as much as 70° from maximum p_π–p_π overlap, and that benzannelation (from the tetradehydrodianthracene framework) would largely destroy any Möbius aromaticity that could be present [38c]. While large [4*n*] and [4*n* + 2]annulenes are not expected to display significant aromatic stabilization or antiaromatic destabilization anyway, the degree of bond length alternation along the Möbius [16]annulene pathway ($\Delta r = 0.120$ Å, difference between the longest and shortest bond lengths) of **1** is rather close to the higher 4*n* + 2π Hückel annulenes, e.g., [14,18,22], ($\Delta r = 0.1$ Å) [39], thus, modest electron delocalization presumably occurs. The loss of π-overlap in nonplanar Hückel and Möbius rings might be less destabilizing than generally supposed, since π-conjugation is largely preserved at small torsional angles, but two-way hyperconjugation is effective at large torsional angles.

Ethylene

Imperfections in typical evaluations of the π-bond energy (see note [40]) of ethylene illustrate a remarkable consequence of two-way hyperconjugation. The common belief that the π-bond of ethylene is much weaker than its C–C σ-bond is based on flawed reasoning. Actually, the reverse is true. As noted above, the rotational barrier of ethylene (65.8 kcal/mol, see Fig. 2b) [8–10] is commonly used to estimate its π-bond energy. But this neglects the two-way hyperconjugation stabilization (ca. 17 kcal/mol [41]) in the D_{2d} rotational TS. When corrected for this effect, the π-bond energy of ethylene (82.8 kcal/mol, 65.8 + 17 = 82.8) is actually higher than the σ-bond energy of ethylene (58.1 kcal/mol), based on the C=C bond energy of ethylene (140.9 kcal/mol, see note [40]) minus the hyperconjugation-corrected π-bond energy (140.9 – 82.8 = 58.1). Contrary to the conventional view, *the π-bond energy of ethylene is greater than its σ-bond energy*! Based on this evaluation, the σ-bond energy of ethylene (58.1 kcal/mol) also is 20.9 kcal/mol weaker than the ethane C–C single bond energy (79.0 kcal/mol, see note [40]) [43]. Note that C–C σ-bond energies cannot be the same in single, double, or triple CC bonds, since the corresponding C–C σ-bond distances are very different. The shorter C_{sp2}–C_{sp2} σ-bond in ethylene (1.33 vs. ca. 1.54 Å for typical alkane C_{sp3}–C_{sp3} σ-bonds), despite having higher *s* character (i.e., more favorable σ-orbital overlap), is weakened by increased internuclear Coulomb repulsion between the close C nuclei [44]. Thus, the short interatomic C–C distance of ethylene results in a strong π-bond, but at the cost of a "compressed" [45], i.e., weaker, C–C σ-bond. The C–C σ-bonds of benzene [45], butadiene (both the central C–C bond and σ-bonds involved in the two C≡C triple bonds), and other highly conjugated molecules are subject to similar "bond compression" problems. Notably, benzene is the *only* neutral aromatic polybenzenoid hydrocarbon with equal CC bond lengths. However, the 1.395 Å CC distances of benzene are too short for a "normal" [45] C–C σ-bond. Although benzene is strongly π-aromatic, Coulson [45], Mulliken [46], and Hornig [47] showed conclusively long ago that the σ-framework of benzene actually suffers from considerable "compressional" strain (ca. 30 kcal/mol). On this basis, benzene is far from being an *unstrained* aromaticity paradigm.

The neglect of two-way hyperconjugation has serious consequences in current interpretations of the energies, geometries, and conformational preferences of many molecules with nonplanar equilibrium structures (or rotational TSs). This results in several textbook-changing propositions. Importantly, unsaturated molecules with nonplanar geometries are not devoid of π-type stabilization! Both *perp*-butadiene and the tub-shaped cyclooctatetraene are far from being unconjugated polyene models as argued above. The π-bond strength of ethylene is actually stronger than its σ-bond. Although deprived of its deserved attention for several decades, Mulliken's [1,4] original two-way hyperconjugation [13] idea (since 1933!) is applicable to many aspects of physical organic chemistry.

HYPERCONJUGATION IN TIGHT SPACES [3]

Historically, hyperconjugation "between saturated groups and double or triple bonds or other saturated groups" has been viewed as "*a mild sort of conjugation*" [1a]. Despite their common physical origin, both geminal (e.g., σ-DC → σ-CA*, Fig. 7a) and vicinal (e.g., σ-DC → σ-CA*, Fig. 7b) hyperconjugations of neutral alkanes are typically weaker than π-conjugation (e.g., π-DC → π-CA*, Fig. 7c). Figures 7a and 7b illustrate geminal and vicinal hyperconjugations as "bond–no-bond" resonance analogs to the usual depiction of π-conjugation in molecules (Fig. 7c).

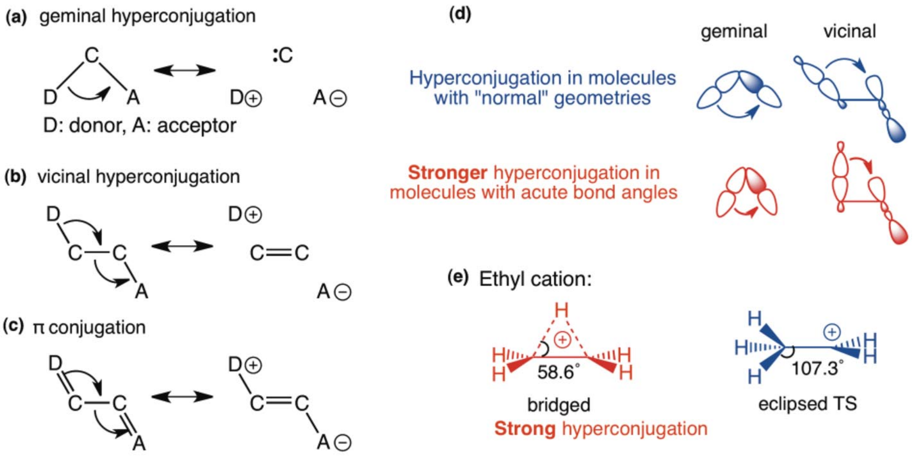

Fig. 7 (a) Geminal hyperconjugation; (b) vicinal HPC; and (c) π-conjugation represented by a "bond–no-bond" resonance (adapted from ref. [48]). (d) Geminal and vicinal HPC in molecules with "normal" vs. acute bond angles. (e) Bridged and eclipsed ethyl cation.

However, the impression that hyperconjugative effects (especially those involving only σ-electrons) are "mild," is largely based on molecules with *normal* unstrained equilibrium geometries and does not consider *extreme* cases. Weinhold and Landis noted that "strong geminal delocalization is rather uncommon in apolar hydrocarbon species, *except in cases of strong angular strain*" [48]. Since hyperconjugation effects involve short-range orbital interactions, large stabilization can arise when the corresponding hyperconjugating donor and acceptor orbitals are constrained to close proximity (i.e., in a *tight space*, see Fig. 7d). The ethyl cation is an extreme example. Despite having two very small 58.6º <HCC angles (see Fig. 7e), the bridged geometry promotes more effective CH → C+ hyperconjugation and is a minimum on the computed $C_2H_5^+$ potential energy surface. The eclipsed classical form has more "normal" <HCC angles (see Fig. 7e) but is only a TS. For the same reason, many molecules (both neutral and charged) with acute bond angles benefit from geminal or vicinal hyperconjugative stabilizations stronger than normally expected as a consequence of their otherwise unfavorable geometry. This section highlights a few representative cases including cyclopropane and several other related systems containing three-membered ring moieties, as well as the cations of some highly strained hydrocarbon cages and bicyclic species.

The cyclopropane story

How and why cyclopropane appears to be more stable than "it ought to be" is a curious problem, as structural and thermochemical features of cyclopropane seemingly contradict all common chemical wisdom (see discussion in ref. [49]). As the smallest cycloalkane ring, cyclopropane is expected by its geometry to have exceptionally high strain. Cyclopropane suffers from angle strain (acute 60º ring

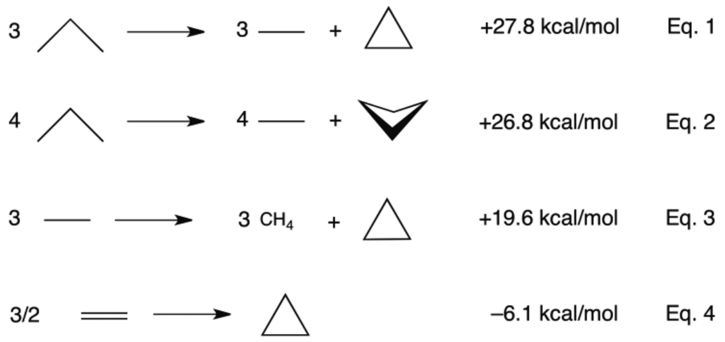

Fig. 8 Conventional strain energy estimates for cyclopropane (eq. 1) and cyclobutane (eq. 2), and alternative ring strain estimates for cyclopropane (eqs. 3 and 4).

angles) [50], eclipsing strain (six fully eclipsed CH's) [51], and the "bent" C–C bonds are exceptionally short (1.512 Å) [52]. However, the conventional strain energy of cyclopropane (+27.8 kcal/mol, i.e., based on eq. 1, see Fig. 8, or by comparing the heats of formation of cyclopropane, +12.8 kcal/mol, to three times the Benson CH_2 group increment, –5.0 kcal/mol [53] or to half the heat of formation of cyclohexane, –29.9 kcal/mol) is nearly the same as cyclobutane (+26.8 kcal/mol, ca. 88° ring angles, eq. 2, see Fig. 8)!

This anomaly was noted when the determination of reliable heats of combustions of alkanes [54] refuted Baeyer's earlier speculation that deviations of the ring angles of assumed planar cycloalkanes from the tetrahedral 109.5° geometry should increase the ring strains of cycloalkanes (C_nH_{2n}) larger and smaller than $n = 5$ (see Fig. 9, dashed line). While none of the cycloalkanes with $n > 5$ were planar and thus had strain energies lower than Baeyer originally expected (see Fig. 9, solid line), the surprisingly low strain of cyclopropane was most puzzling (see Fig. 9, solid line). Based on simple force constant calculations [55], Cremer et al. projected the total strain energy of cyclopropane to be at least

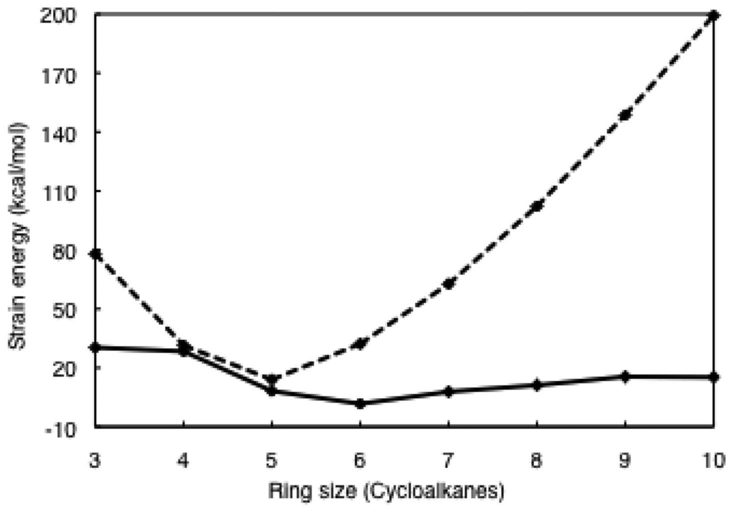

Fig. 9 Estimated strain energies computed at MP2/6-311+G** (no ZPE) for assumed planar cycloalkanes based on Baeyer's angle strain theory (dashed line) and the conventional strain energies of cycloalkanes (solid line) (all except for cyclopropane have nonplanar equilibrium geometries) evaluated by the conventional equation: $nC_3H_8 \rightarrow nC_2H_6 + C_nH_{2n}$.

75 kcal/mol [56]. On this basis, the conventional ring strain of cyclopropane (27.8 kcal/mol) is 48 kcal/mol too low [57]! Depending on the reference standard chosen, the ring strain of cyclopropane also could be evaluated by a bond separation reaction (eq. 3, +19.6 kcal/mol, see Fig. 8) [58,59]. “Even a ‘negative’ strain energy of cyclopropane” (eq. 4, –6.1 kcal/mol, see Fig. 8) can be deduced [59] by a direct comparison with ethylene (viewed as the simplest olefinic “dimethylene” ring, based on Walsh’s sp^2 model of cyclopropane). Nevertheless, none of these estimates are consistent with the anticipated high ring strain of cyclopropane. The “missing ring strain” of cyclopropane also is unique, as many other three-membered rings exhibit rather “normal” (i.e., much higher) conventional strain energies relative to their four-membered ring analogs, e.g., cyclopropene (53.8 kcal/mol) vs. cyclobutene (30.0 kcal/mol) [53], perfluorocyclopropane (53.7 kcal/mol) vs. perfluorocyclobutane (24.8 kcal/mol) [60], and silacyclopropane (38.3 kcal/mol) vs. silacyclobutane (17.0 kcal/mol) [61].

Obviously, effects other than angle strain must contribute to the nearly identical ring strain of cyclopropane vs. cyclobutane. Either cyclopropane is unusually stabilized or cyclobutane is destabilized (or both). Several possibilities including σ-aromaticity [57] and stronger C–H bonds [62] in cyclopropane, as well as cross-ring 1,3-CC repulsion in cyclobutane [63] have been considered, but none of these effectively rationalize the ca. 50 kcal/mol lack of strain in cyclopropane. Dewar’s speculative *σ-aromaticity* idea, that delocalization of the six σ-electrons in cyclopropane being “isoconjugate” with the cyclic six π-electron delocalization of benzene might be aromatically stabilizing [57], was the most attractive rationalization. Cremer et al. noted that the accumulation of electron density towards the cyclopropane ring center might relieve some angle strain in cyclopropane via *surface delocalization* [56]. Nevertheless, direct evaluations of the σ-aromaticity hypothesis using various lines of reasoning and degrees of sophistication all have resulted in low or negligible estimates of the putative σ-aromatic stabilization energy of cyclopropane [60,64–67]. Upfield ^1H chemical shifts [68], exalted magnetic susceptibilities [69], computed negative isotropic nucleus independent chemical shifts (NICS) at the cyclopropane ring center [70], and computed induced diatropic ring currents [71] were proposed to support the possibility of σ-aromaticity in cyclopropane. However, Lazarretti et al.’s [72] detailed assessment of the diatropic cyclopropane σ-ring current revealed several features incompatible with the existence of σ-aromaticity and refuted “evidence for strong diatropism, and therefore σ-aromaticity in the cyclopropane molecule.” Direct evidence for σ-aromaticity in cyclopropane has not been found!

Alternatively, Inagaki et al. [60] proposed that *local* geminal σ_{CC}–σ_{CC}^* interactions might relax the ring strain of cyclopropane. In effect, this possibility recasts Dewar’s σ-aromaticity argument without invoking any special cyclic effects. Inagaki et al. noted that geminal σ_{CC} and σ_{CC}^* hybrid orbitals with more *p* character (e.g., $sp^{4.0}$ as in cyclopropane) have much weaker antibonding interactions compared to those with higher *s* character (e.g. $sp^{2.9}$ in propane, $sp^{3.2}$ in cyclobutane, $sp^{3.5}$ in perfluorocyclopropane) [60]. Thus, “as the bond angle [of cyclopropane] is acute, the antibonding property is depressed, leading to the relaxation of the angle strain expected from the bond angle for cyclopropane” [60]. A slightly different perspective led to the same conclusion. Weinhold and Landis examined the angular dependence of *geminal* $\sigma_{CC} \rightarrow \sigma_{CC}^*$ electron *delocalization* effects and concluded “whereas geminal stabilizations are less than 1 kcal/mol for larger [cycloalkane] rings ($n \geq 4$, $\theta_{ccc} \geq 90°$), these interactions become *strongly* stabilizing at the $\theta = 60°$ geometry of cyclopropane” [48]. Based on NBO second-order perturbation analysis, the geminal $\sigma_{CC} \rightarrow \sigma_{CC}^*$ interactions in cyclopropane total 49.2 kcal/mol (8.2 kcal/mol for each of the interactions, six in all), but only total 4.0 kcal/mol (0.5 kcal/mol per interaction, eight in all) in cyclobutane (at HF/6-311+G**) (see Fig. 10a). Cyclopentane and cyclohexane also display small geminal $\sigma_{CC} \rightarrow \sigma_{CC}^*$ interactions because of their relatively “normal” geometries (see Fig. 10a). *Geminal hyperconjugation stabilization in cyclopropane is enormous because of its strained skeleton!* On the other hand, the $\sigma_{SiSi} \rightarrow \sigma_{SiSi}^*$ interactions are small regardless of the SiSiSi angle (hence, the strain energies of silicon rings follow Baeyer’s expectations) [48], since σ-SiSi bonds don’t hyperconjugate as effectively as σ-CH or σ-CC bonds. While computed NBO interactions energies tend to overestimate electron delocalization effects in molecules and thus can serve only as an upper bound for the actual stabilization energies, the qualitative implica-

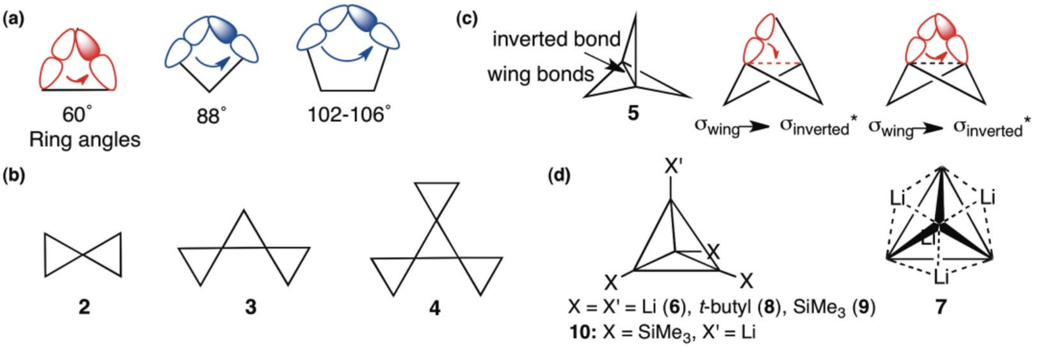

Fig. 10 (a) Schematic representation of geminal hyperconjugation in cyclopropane, cyclobutane, and cyclopentane; (b) triangulanes (**2–4**); (c) geminal hyperconjugation in [1.1.1]propellane (**5**); (d) tetrahedrane derivatives (**6–10**).

tion of Weinhold [48] and Inagaki [60] et al.'s independent findings are clear and consistent: geminal hyperconjugation effects are strongly angular dependent and are much more stabilizing for molecules with small CCC angles. The combined stabilization of geminal hyperconjugation (49.2 kcal/mol, as an upper bound estimate) and CH bond rehybridization (11.7 kcal/mol) [62] in cyclopropane are likely the chief reasons for its unusually low conventional ring strain.

But why do other cyclopropane analogs (e.g., perfluorocyclopropane) exhibit relatively normal (high) strain energies? Geminal hyperconjugations are not just angular dependent but their magnitudes depend also on electronic (i.e., σ-inductive) effects, as implied by Inagaki's hybridization argument [60]. Electronegative substituents (e.g., F) diminish geminal $\sigma_{CC} \rightarrow \sigma_{CC}{}^*$ hyperconjugation interactions in cyclopropane by reducing effective σ_{CC}–$\sigma_{CC}{}^*$ orbital overlap [60,73], but electropositive substituents (e.g., Li, BeH, $SiMe_3$, cyclopropyl) have the opposite effect [73]. In agreement, NBO computations disclose that the geminal $\sigma_{CC} \rightarrow \sigma_{CC}{}^*$ interactions in perfluorocyclopropane only total 15.6 kcal/mol (2.6 kcal/mol per interaction, six in all) but total 58.2 kcal/mol (9.7 kcal/mol per interaction) in $C_3(BeH)_6$ (at HF/6-311+G**) [73]. Perfluorocyclopropane is highly strained due to the lack of effective geminal hyperconjugation stabilization to compensate for its angle strain. Conversely, cyclopropane (and tetrahedrane, see below) analogs bearing effective electropositive substituents benefit from substantial geminal hyperconjugation and can have exceptionally low strain energies.

The triangulanes (e.g., **2–4**, see Fig. 10b) are an interesting example. Novak found the triangulanes C_5H_8 (**2**), C_7H_{10} (**3**), and C_9H_{12} (**4**, [3]rotane) to be increasingly less strained than cyclopropane [74] and commented, "the strain energies of cyclotriangulanes are much smaller than previously estimated which makes them more easily achievable synthetic targets than earlier thought". Several larger spirocyclopropane derivatives have been synthesized [75]. On the same basis, [1.1.1] propellane (**5**) also is subject to strong geminal hyperconjugation (see Fig. 10c) [60]. Despite having three cyclopropane rings and a short inverted bridgehead–bridgehead bond (ca. 1.60 Å [76]) (characterized by Wu et al. as a charge shift bond) [77], **5** is surprisingly thermochemically stable [78] (albeit not very persistent kinetically, i.e., **5** isomerizes to 3-methylenecyclobutene at high temperatures). NBO computations reveal substantial geminal hyperconjugative interactions for both $\sigma_{CCwing} \rightarrow \sigma_{CCinverted}{}^*$ (16.6 kcal/mol per interaction) and $\sigma_{CCwing} \rightarrow \sigma_{CCwing}{}^*$ (19.9 kcal/mol per interaction) (at HF/6-311+G**) (see Fig. 10c). Although viewed from a rather different perspective, Wu et al. surmised that "analogues of [1.1.1]propellane, in which the CH_2 groups at the wings are replaced by powerful electron donors, such as NH, O, and S" could have even shorter "inverted" C–C bonds [77]. Such predictions agree with the expectation that electropositive substituents could promote geminal hyperconjugation and lead to a shorter bridgehead–bridgehead bond in **5**.

Tetrahedrane does not have "super σ-aromaticity," as has been speculated [70b]. Although the importance of geminal hyperconjugation had not yet been recognized in the 1970s, Dill, Greenberg, and

Liebman's comprehensive study of substituent effects on the strain energies of several rings and cages noted a remarkable strain reduction effect for lithium substituents [79]. They commented, "the most striking result in the lithium series is the enormous strain reduction calculated for the idealized, corner-lithiated tetralithiotetrahedrane (**6**) (see Fig. 10d) – a result providing some reason for optimism over the possible synthesis of C_4Li_4" [79]. Shortly before this study, Rauscher and Schleyer et al. had attempted to synthesize C_4Li_4 [80] and demonstrated computationally that the face-lithiated minimum (**7**) (see Fig. 10d) was essentially strain free [81]. Importantly, this does not imply that C_4Li_4 is thermochemically stable in the absolute sense, but merely indicates that it is *more stable than it ought to be* in view of its highly unfavorable geometry (12 60º CCC angles). Since electropositive substituents promote geminal hyperconjugation, while electronegative substituents have the opposite effect, the computed NBO geminal $\sigma_{CC} \rightarrow \sigma_{CC}^*$ interaction energies (at HF/6-311+G**) for **7** (165.5 kcal/mol), **6** (153.6 kcal/mol), tetrahedrane (132.0 kcal/mol), and perfluorotetrahedrane (69.9 kcal/mol) follow the order: **7** > **6** > tetrahedrane >> perfluorotetrahedrane. In sharp contrast, such interactions are tiny in cubane (less than 0.5 kcal/mol per interaction, since the wider 90º CCC angles are not acute enough to promote similarly enhanced geminal hyperconjugation). We stress again that the *theoretical* NBO-computed orbital interaction energies are not expected to be directly comparable to actual experimental values, but the trends are noteworthy. While the parent tetrahedrane has never been isolated, the known tetrahedrane analogs, e.g., tetrakis(*tert*-butyl)tetrahedrane (**8**) [82], tetrakis(trimethylsilyl)tetrahedrane (**9**) [83], tris(trimethylsilyl)tetrahedranyllithium (**10**) [84], and possibly tetralithiotetrahedrane [80], inevitably owe part of their viability to the strong geminal hyperconjugation substantiated by their electropositive substituents (see Fig. 10d). Those with bulky substituents benefit from additional (steric) kinetic persistence [82].

Contrary to Baeyer's 1885 speculation [50], angular strain does not preclude the accessibility of the three-membered ring motif. Despite their unfavorable geometric appearance, these small rings are stabilized electronically by geminal hyperconjugations in tight spaces. Many natural products and synthetically available molecules have cyclopropane cores [86].

Bridgehead reactivities of strained hydrocarbons

The solvolytic reactivities of hydrocarbon bridgeheads pose another interesting consequence of hyperconjugation in tight spaces. Following the pioneering work of Bartlett and Knox [87], the rates of solvolysis at the bridgehead positions of hydrocarbon cages were noted to correlate inversely with the size of the bridged ring system [88]. As carbonium centers usually prefer planar local geometries, the S_N1 solvolysis rates at small hydrocarbon cage bridgehead positions are inhibited by the reluctance of developing a positive charge at the pyramidalized positions. Conversely, the relatively "flatter" bridgehead carbons of larger hydrocarbon cages have higher reactivity. Based on molecular mechanics computations, Bingham and Schleyer [89] (later refined by Müller et al. [90]) established an excellent linear correlation between the solvolysis rates of bridgehead derivatives and the corresponding hydrocarbon-cation strain energy difference. This important contribution provided a reliable means of predicting the solvolytic rates of wide ranges of hydrocarbons. Following this principle, the relative solvolytic rates of *tert*-butyl bromide, 1-bromoadamantane **11** (X = Br), 1-bromobicyclo[2.2.2]octane **12**(X = Br), and 1-bromonorbornane **13** (X = Br) are in the order: $1 > 10^{-3} > 10^{-6} > 10^{-13}$ [91,92]. However, extensions of this relationship failed to hold for hydrocarbon cages with extremely compact geometries [93].

The experimental solvolysis rates of several bicyclo[*n*.1.1]alkyl halides **14–16** and cubyl derivatives **17–18** (see Fig. 11) are far greater than expected on the basis of the high pyramidal bridgehead strain of the resulting carbocation intermediates. Thus, 1-chlorobicyclo[1.1.1] pentane **14** (X = Cl) reacts three times faster than *tert*-butyl chloride and 10^{14} times faster than 1-chloronorbornane **13** (X = Cl) [94]. 1-Bromobicyclo[2.1.1]hexane **15** (X = Br) reacts 10^7 times faster than 1-bromonorbornane **13** (X = Br) [92]. 1-Bromobicyclo[3.1.1]heptane **16** (X = Br) is eight times more reactive than *tert*-

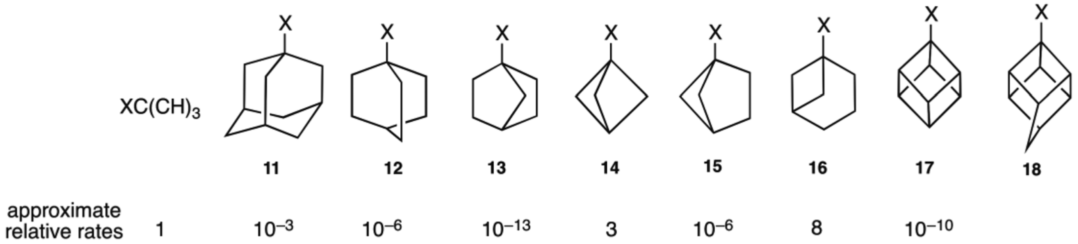

Fig. 11 Bridgehead-substituted hydrocarbon cages and approximate relative solvolysis rates.

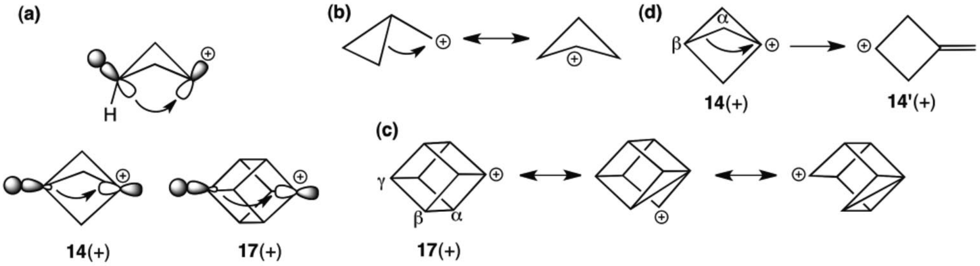

Fig. 12 (a) Transannular through-space charge stabilization in the cyclobutyl cation, **14**(+) and **17**(+); (b) the cyclopropylcarbinyl-cyclobutyl cation resonance; (c) resonance forms stabilizing the cubyl cation; (d) the rearrangement of **14**(+) to **14** (+).

butyl bromide [95]. **17** (X = OTs), **17** (X = OTf) [96], and the 4-homocubyl bromide **18** (X = Br) [97] also display enhanced solvolytic reactivities compared to their 1-norbornyl analogs. Wiberg and Williams conjectured that the high solvolytic reactivities of **14** (X = Cl) and **15** (X = Br) might be attributed to the relief of ring strain, since both led only to rearranged products. However, **16** (X = Br) solvolyzed both to rearranged and unrearranged products, while **17** and **18** yielded only unrearranged products. Alternatively, these authors noted the extremely short C1–C3 distance of the parent bicyclo[1.1.1]pentane (1.85 Å) **14** (X = H) [98] and suggested that cross-ring transannular interactions, much like that proposed for explaining the fast solvolysis of equatorial vs. axial substituted cyclobutyl systems [99], might stabilize the developing **14**(+) and contribute to the fast solvolysis of **14** (see Fig. 12a) [92]. On the same basis, **15**(+)–**18**(+) could be stabilized by similar transannular charge delocalization, since their bridgehead carbonium centers all involve cyclobutyl rings.

Della et al. noted that both **14**(+) and **15**(+) exhibited extremely short C1–C3 (1.537 Å) and C1–C4 (1.690 Å) nonbonded cross-ring distances (RHF/6-31G*) indicative of extensive through space interaction [93], and commented later on that **15**(+) “derives favorable thermodynamic stabilization from cross-ring σ-hyperconjugation overlap of the empty p-orbital on the charged carbon atom with the back lobe of the C–H bonding orbital of the other bridgehead carbon” [100]. Similarly, Moriarty et al. attributed the rate retardation of several 4-substituted **17** (OTs) species to “a highly effective transannular transmission of the polar effect of the positive end of the C–X dipole upon the incipient carbocationic center” [101]. However, Eaton et al. argued that similar polar field effects in 3-substituted-adamantyl halides led to far less rate enhancements than those observed for the cubyl systems, and thus the transannular “charge delocalization mechanism is probably unimportant for [the] cubyl cation” [91]. Furthermore, the rate-retarding effect of a methyl substitution at the C4 position of **17** [96,101] was taken as evidence against the transannular stabilization argument.

Several research groups [96,97,101] considered the possibility of nonclassical charge delocalization stabilization. Akin to the cyclopropylcarbinyl-cyclobutyl cation resonance (see Fig. 12b) [103], the positive charges in **17**(+) (see Fig. 12c) [96,102] and **18**(+) [97] could be depleted through a similar mechanism. Hrovat and Borden reported that "the additional finding of a positive bond order between the electron deficient p-orbital at the cationic carbon and the p-orbital, aligned with it, at each of the three beta carbons suggests that some stabilization of **17**(+) comes from delocalization of the electrons in the α,β and β,γ C–C bonds" (see Fig. 12c) [102]. We note that the rearrangement of **14**(+) to **14** (+) anticipates similar electron delocalization involving the α,β C–C bonds of **14**(+) (see Fig. 12d). The unusually long α,β C–C bonds of **14**(+) (1.59–1.61 Å, based on various computation methods) [104], **17**(+) (1.583 Å), and the C_2–C_3 bond of **15**(+) (1.64–1.66 Å) also imply effective delocalization from these C–C bonds to the cationic center, which might be more generally viewed as a vicinal $\sigma_{C\alpha C\beta}/\sigma_{C2C3} \rightarrow p^*$ hyperconjugation (see Fig. 13a). Further support for this possibility stems from more recent computational studies which established that several cyclobutyl-containing systems, e.g., the parent cyclobutane (see Fig. 13b) [105], the cyclobutadienyl dication (see Fig. 13c), and other puckered 2π-electron four-membered rings [106], have dominant vicinal ring $\sigma_{CC} \rightarrow p^*$ hyperconjugations. Indeed, NBO computations confirm that vicinal $\sigma_{C\alpha C\beta}/\sigma_{C2C3} \rightarrow p^*$, rather than transannular $\sigma_{CH} \rightarrow p^*$ (Fig. 12a), interactions are the key factors stabilizing **14**(+) and **17**(+) (see Fig. 13a). Hence, the solvolytic rates of **14–18** rely on a delicate balance between the opposing geometric strain (which retards solvolytic rates) and electronic stabilization (which enhances solvolytic rates) (see Fig. 13a). As the local bridgehead pyramidalization angles increase for smaller strained cages, so do the strengths of stabilizing vicinal $\sigma_{C\alpha C\beta}/\sigma_{C2C3} \rightarrow p^*$ interactions, as the hyperconjugating $\sigma_{C\alpha C\beta}/\sigma_{C2C3}$ bonds are forced to closer proximity with the cationic center.

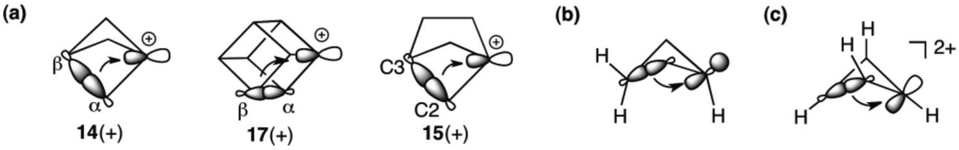

Fig. 13 Through-bond vicinal $\sigma_{CC} \rightarrow p^*$ hyperconjugation in (a) **14**(+), **17**(+), and **15**(+); (b) cyclobutane; (c) and the cyclobutadienyl dication.

In light of Coulson's famous admonition "give me insight, not numbers" [107], molecules that benefit from enormous hyperconjugation in tight spaces exemplify the reverse case where traditional chemical intuition fails to give the correct "insight", while the actual "numbers" estimating these hyperconjugative effects do matter and are important for properly interpreting their chemistry.

Other larger hydrocarbon cages, e.g., **19**(+), **20**(2+), and **11**(+), benefit from similar vicinal $\sigma_{CC} \rightarrow p^*$ hyperconjugative interactions (Fig. 14). At the extreme, the much debated structure of the 2-norbornyl cation **19**(+) [108] either viewed as nonclassical σ-bridging species [109], a π-complex [110], or a rapid equilibrium of two classical structures (via a Wagner–Meerwin type rearrangement) [111], can also be interpreted as a vicinal $\sigma_{CC} \rightarrow p^*$ hyperconjugation between the C1–C6 bond and the incipient cationic center at C2 upon the solvolysis of 2-norbonyl derivatives (see Fig. 14a). Because of such *hyperconjugative* anchimeric (neighboring group) assistance, the exo isomers of 2-norbornyl arenesulfonates (**19**) react much more rapidly than the endo isomers [112] (although the possibility that the endo solvolysis is sterically retarded also has been considered [113]). The same argument might be applied, in place of cross-ring transannular interactions, to rationalize the faster solvolytic rates of equatorial substituted cyclobutyl derivatives (see Fig. 13b). Despite having two positive charges at each of the bridgehead positions, **20**(2+) exhibits an extremely short cross-ring C1–C4 distance (2.163 Å) compared to that of the parent bicyclo[2.2.2]octane (2.594 Å) [114]. This certainly could not be explained by any transannular effect, since both of the bridgeheads are positively charged. Olah et al. commented, "the small 1,4 distance in **20**(2+) is due to hyperconjugative transfer of electron density to the cationic centers which then participate in symmetry allowed 1,4-bonding" [114] (see Fig. 14b). The 1-adamantyl cation **11**(+), one of the first isolated carbocations in superacid media [115], also owes its peculiar geo-

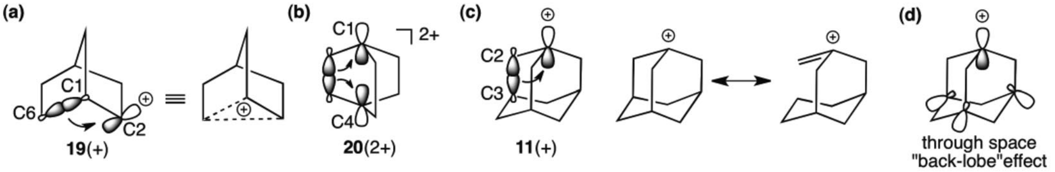

Fig. 14 Vicinal $\sigma_{CC} \rightarrow p^*$ hyperconjugation in (a) the nonclassical 2-norbornyl cation **19**(+); (b) 1,4-bicyclo[2.2.2]octyl dication **20**(2+); and (c) the 1-adamantyl cation **11**(+). (d) Through-space orbital interactions in **11**(+).

metric and spectroscopic features to "carbon–carbon [$\sigma_{C2C3} \rightarrow p^*$] hyperconjugative stabilization" (see Fig. 14c) as "the major mode of cation stabilization" [116], rather than homoconjugation between the cationic center and the backside lobes of the remaining three bridgehead CH bond orbitals [115] (see Fig. 14d). The unusually deshielded ^{13}C NMR shifts of C2 (65.7 ppm) and C3 (86.8 ppm) [115,117] as well as the long C2–C3 bond of **11**(+) (1.590 Å [116]) corresponding to the resonance structure depicted in Fig. 14c [115] are supportive. While **11**(+), **19**(+), and **20**(2+) are all relatively unstrained compared to **14–18**, and do not necessarily have *tight spaces* [3], constraints from the rigid cage geometries help promote effective vicinal $\sigma_{CC} \rightarrow p^*$ hyperconjugation.

OUTLOOK

Hyperconjugation is not just a mild sort of conjugation, as Alabugin et al.'s review [4] also emphasizes, but in many instances, such as those discussed here, can have surprisingly large stabilizing effects. The ideas presented in this review, that nonplanar polyenes can benefit from two-way hyperconjugation stabilization and that molecules with condensed geometries might be stabilized effectively via hyperconjugation in tight spaces, extend conventional chemical wisdom and have far-reaching prospects for the chemistry of functional nonplanar polyenes as well as strained rings and cages, many of which find important usage in more applied fields of science. At the didactic level, we wish to raise the awareness of teaching students these new perspectives and conceptual advancement of old topics. This challenge applies to scientific progress generally.

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ated fragments. Following the valence bond definition for a chemical bond, computed "in situ bond strengths" provide a "direct measure of the stabilization associated to the exchange of the two electrons in a covalent valence bond structure" "complemented by the resonance energy stabilization owing to the mixing of ionic structures" [77]. The three procedures described above differ drastically; e.g., the σ-C–C bond energy, bond dissociation energy, and in situ σ-bond strength, of ethane are: 79.0 kcal/mol (see above; or 86.6 kcal/mol in ref. [42]), 96.1 kcal/mol [77], and 138.5 kcal/mol [77], respectively. This discussion will be amplified in a separate paper.

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