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In-Plane Aromaticity and Trishomoaromaticity: A Computational Evaluation

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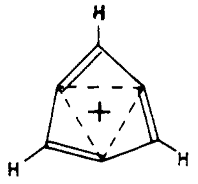
In-plane $4n + 2$ aromaticity in hydrocarbons containing radial p orbitals is predicted in suitably constituted uncharged polyolefinic systems. Several criteria were employed to investigate aromaticity in [n]peristylapolyenes (n = 3–5), p-[$4^2.5^8$]hexadecahedrapolyenes, dodecahedrapolyenes, and tetraquinapolyenes by using Allinger's MMP2 program. In the most favorable cases, after correction for strain effects, modest but significant π stabilization energies are indicated. MNDO semiempirical calculations also indicate a cyclic conjugated dodecahedrapentaene to be aromatic. In addition, the possibility of trishomoaromaticity in known and several previously unknown trienes was investigated, but these are no more than slightly favorable. Geometrical restrictions imposed by the σ framework in such cases prevent adequate overlap of the π orbitals.

In-plane aromaticity was recognized by Chandrasekhar et al. to be important in the $C_6H_3^+$ cation (**1**); the three (largely p) atomic orbitals (AOs) interacting in the molecular plane have the same symmetry properties as those in the cyclopropenium ion.[1] Ion **1** was termed "double aromatic" because it contains two orthogonal sets of p AOs: the aromatic benzenoid 6-π electron system as well as the "σ" type in-plane two-electron homoaromatic system. Later, Fukunaga et al. termed systems with an annulene perimeter and an in-plane three-center two electron bond "trefoil aromatics",[2] but no system has been found calculationally where the trefoil geometry is preferred. For example, compounds **2** and **3** are approximately 100 and 37 kcal/mol less stable than their respective valence isomeric structures, **4** and **5** (MNDO and MINDO/3).[3]

A number of related molecules also have been calculated:[4] $C_{10}H_5^-$ (D_{5h}) (**6**), with 10 π and 6 σ electron systems, $C_{10}H_5Li$ (D_{5h}), a similar compound with a lithium cation in the center, and C_8H_4 (**7**), which has the potential of forming a 10 π and 2 σ double aromatic (instead of the 8 π and 4 σ double antiaromatic) arrangement of interacting p AOs. Except for **1**, none of these isomers with in-plane aromaticity appear to be promising energetically. However, only *homoconjugative* overlap is possible in these systems and this might be responsible.

In-plane pp cyclic conjugation may provide greater stabilization. Extensive but preliminary calculations were carried out on rings only comprised of carbon atoms.[5] These planar C_{2n} (n = 3–6) molecules have two orthogonal conjugating p systems (Figure 1). At the limited levels of ab initio theory employed (STO-3G plus 6-31G for the smaller C_{2n} compounds), all the C_{2n} molecules seem to be more stable in linear diradical than in cyclic arrangements.



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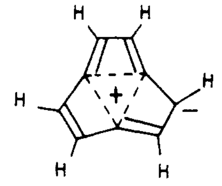

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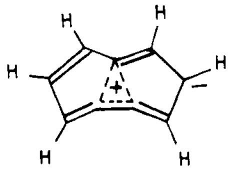

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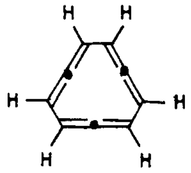

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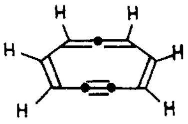

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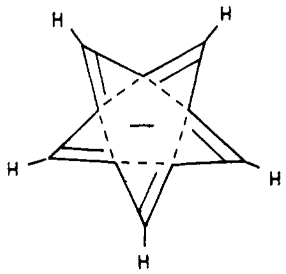

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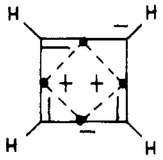

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Although the possibility of in-plane pp conjugation in hydrocarbons has been largely ignored, neutral[6] trishomoaromaticity has received appreciable attention.[7-13] Theoretical and experimental studies of *cis,cis,cis*-1,4,7-cyclononatriene (**8**), triquinacene (**9**),[10] C_{16}-hexaquinacene (**10**),[11] *cis,cis,cis*-1,5,9-cyclododecatriene (**11**),[12] and tetracycle[8.2.2.$2^{2,5}$.$2^{6,9}$]-1,5,9-octadecatriene (**12**)[13] have sought to evaluate the extent of trishomoconjugation. Photoelectron spectroscopy (PES) shows that there is some interaction between double bonds in **8**, **9**, **10**, and **12**,[9c,10b,11b,13] but X-ray analysis, ^{1}H NMR spectroscopy, and the heats of hydrogenation fail to reveal any significant stabilizing effects due to trishomoaromaticity.[9-13] Indeed, the heats of formation of the delocalized homobenzene valence

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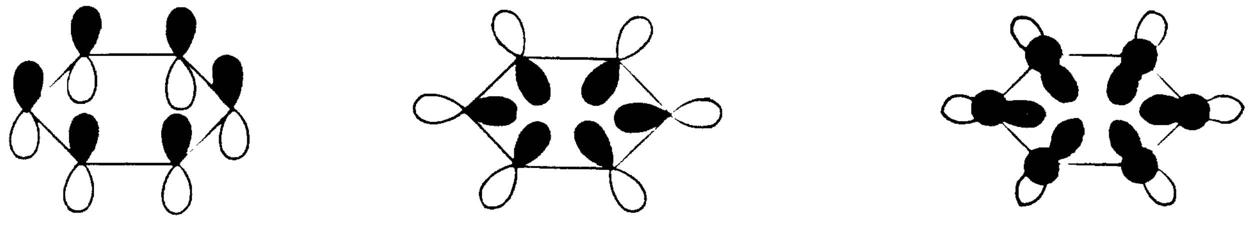
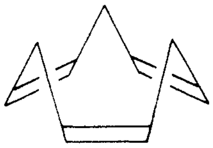


pi sigma orthogonal

Figure 1. Possible overlap of cyclic p atomic orbitals.

tautomers of **8** and **9** are 63.0 and 81.0 kcal/mol higher in energy than those of the localized triene structures (MINDO/3).[8b] Several groups of investigators have concluded that the σ-type overlap of the π orbitals in **8–10** not only is ineffective but is destabilizing due to π–π repulsive interactions.[11a,14] In fact, neutral "trishomoaromaticity" as a stabilizing phenomenon has been ruled out.[11b]



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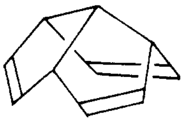

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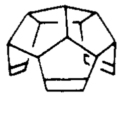

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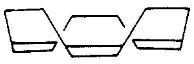

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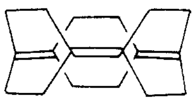

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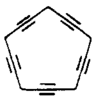
The [*n*]pericyclynes are another class of compounds which might exhibit in-plane homoconjugation. Extensive interaction between the π MOs of [5]pericyclyne (**13**) has been observed by Scott et al (PES).[15] Based on MNDO calculations, Dewar's group attributed this interaction to hyperconjugation in the π system and homoconjugation in the σ system.[16] MNDO calculations of [3]pericyclyne (**14**) also indicate in-plane through-space interactions between the acetylene units. However, tricyclopropabenzene (**14a**), the aromatic valence tautomer of **14**, has a heat of formation 60.7 kcal/mol *greater* than that of **14**.[16] Houk et al. reported that cross-ring in-plane π–π interaction in the related 1,5,9-cyclododecatriyne (**15**) probably is destabilizing.[17] The [*n*]beltenes **16** also possess radially oriented p AOs. Homoconjugation has not been investigated in these molecules; however, MM2 calculations show them to be stable.[18]



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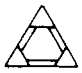

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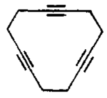

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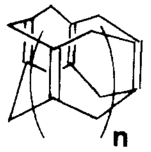

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Hydrocarbons where one or both of the two orthogonal p AO systems are antiaromatic[19] also have been investigated. Compounds **17** and **18** which have antiaromatic (i.e., $4n$ electron) π systems and possibly homoaromatic in-plane p AO overlap exhibit little splitting of the in-plane π orbitals due to mixing with the σ skeleton (PES).[20] Compounds **19** and **22**, with both p AO systems being antiaromatic, display in-plane interaction between the π molecular orbitals (MOs) of the triple bonds (PES).[20b,21,22]

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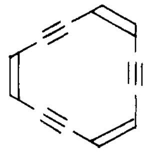
MNDO calculations predict that **23** also should have in-plane interactions.[16] Compounds containing multiple triple bonds with silicon spacer groups (SiH_2 and $Si(CH_3)_2$) have been investigated with regard to possible in-plane interaction of the π MOs; however, any homoconjugation of the π MOs is obscured by extensive hyperconjugation with the σ skeleton.[23]



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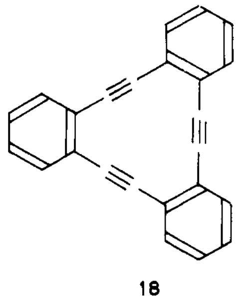

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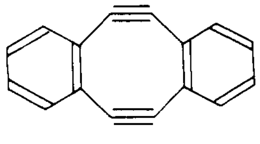

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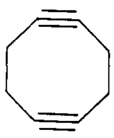

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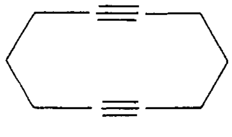

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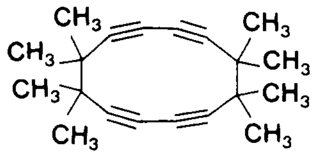

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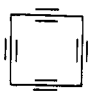

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We have investigated computationally a series of hydrocarbons with conjugated p orbitals arranged to permit in-plane σ aromaticity. For conjugated valence tautomers to be formed, the stabilizing p electron delocalization must be more important energetically than any concurrent increase in the strain energy.[14,24] Therefore, for in-plane pp aromaticity to exist in hydrocarbons, the carbon framework must facilitate delocalization of the p AOs. Systems with ideal-appearing σ skeletons which we have explored include the [*n*]peristylanes, *p*-[4^2.5^8]hexadecahedrane, dodecahedrane, and tetraquinacane (Figure 2).[25] Systematic investigation of in-plane and radial pp conjugation was done by introducing double bonds progressively around the perimeters of these polycyclic frameworks. We also investigated the possibility of in-plane trishomoaromaticity computationally in five new trienes (Figure 3) as well as in the known compounds **8**–**12**.

Method

The MMP2 empirical force field program of Allinger[26] was employed. This program separates molecules mathematically into a σ skeleton and a p AO system and treats these more or less independently. A SCF calculation on the p AOs provides the force constants to be used in the force field calculations. Bond orders, resonance integrals, bond energies (the energy due to the bonding of p AOs), and orbital splitting energies are obtained as standard output from the SCF calculations of the p AOs. This information, in addition to the heats of formation and strain energies, is useful in assessing the degree of conjugation and of aromaticity in polyene systems.

Another feature of the MMP2 program is particularly suited to studying homoconjugation. The normal MMP2 SCF cycle recognizes only *conjugated* interactions; therefore, molecular structures are determined first by *excluding* unconjugated pp interactions (e.g., between double bonds in homoconjugated systems). By then specifically including such unconjugated pp interactions (NBI) in the SCF cycle, the structural and energetic changes due to homoconjugation can be assessed.

In addition to the MMP2 calculations, the MNDO semiempirical method[27] was employed on one dodecahedrapentaene cyclic conjugated p system where MMP2 results showed favorable aromatic characteristics.

Results and Discussion

In section A we examine the possibility of in-plane trishomoaromaticity in **8**–**12** and in several compounds which have not yet been prepared (Figure 3). In part B we evaluate in-plane and radial conjugation and aromaticity in the [*n*]peristylapolyene, *p*-[4^2,5^8]hexadecahedrapolyene, dodecahedrapolyene, and tetraquinapolyene systems (Figures 4–7). We employ several criteria to assess "aromaticity"; comparison of heats of hydrogenation, corrected for strain energy differences; resonance integrals; resonance energies; bond orders; and the degree of bond alternation.

A. Trishomoaromaticity. After reevaluating the extent of the interactions among the double bonds in **8**–**12**, we explored molecules **24**–**28** where trishomoaromaticity might be more favorable (Figure 3). The calculated and available experimental data for these compounds are summarized in Table I. The energetic and geometric consequences of trishomoconjugation were investigated by first treating the three olefins as isolated units and then allowing homoconjugative interactions between the π MOs to take place (i.e., by turning homoconjugation "on" (inclusion of NBI) and "off" in the MMP2 program). The MMP2(NBI) calculated geometries reproduce the available experimental values well; with **8** and **9** the agreement is better than the MINDO/3 results (Table I).

The energetic effects of trishomoconjugation are summarized in Table II. These values are differences between the results of calculations which allow homoconjugative interactions to occur and those with isolated double bonds (i.e., MMP2(NBI) value − MMP2 value). The presence of trishomoconjugation in a molecule depends on whether interaction between the π MOs is favorable ($\Delta E_{el} < 0$) and whether this stabilization is opposed by any increase in strain energy of the σ framework (Δ strain energy > 0). Inclusion of nonbonding pp interactions (NBI) in the SCF cycle increases the heat of formation of **8** and **12** (0.2 and 1.9 kcal/mol) and results in only a small decrease in the heat of formation of **9**–**11** (−1.3 to −0.3 kcal/mol, Table II). Hence, the increase in strain energy opposes and thus prevents any large stabilization due to trishomoconjugation. Repulsive steric interactions between the olefinic hydrogens and bond angle deformations, resulting from

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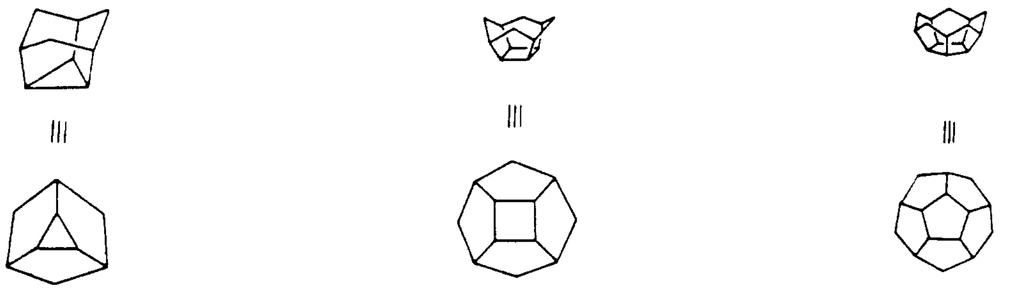
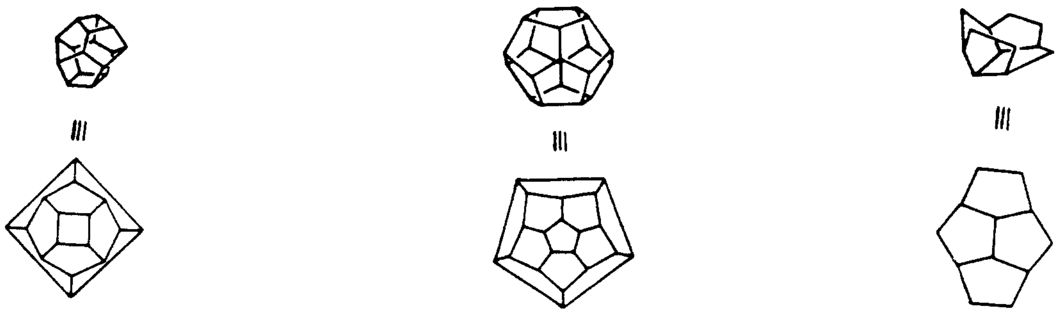
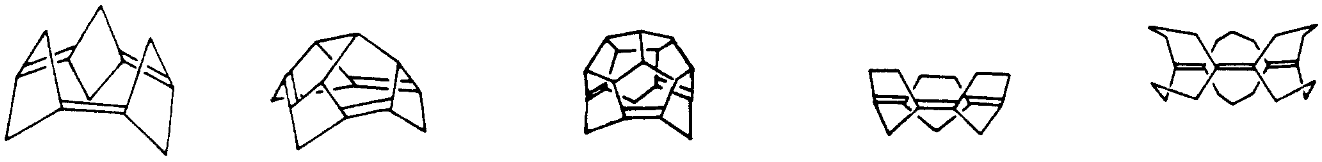


[3]peristylane [4]peristylane [5]peristylane



p-[4².5⁸]hexadecahedrane dodecahedrane tetraquinacane

Figure 2. Polycyclic systems used to investigate in-plane and radial conjugation. The planar graph representations used in Figures 4–7 also are shown.



24 25 26 27 28

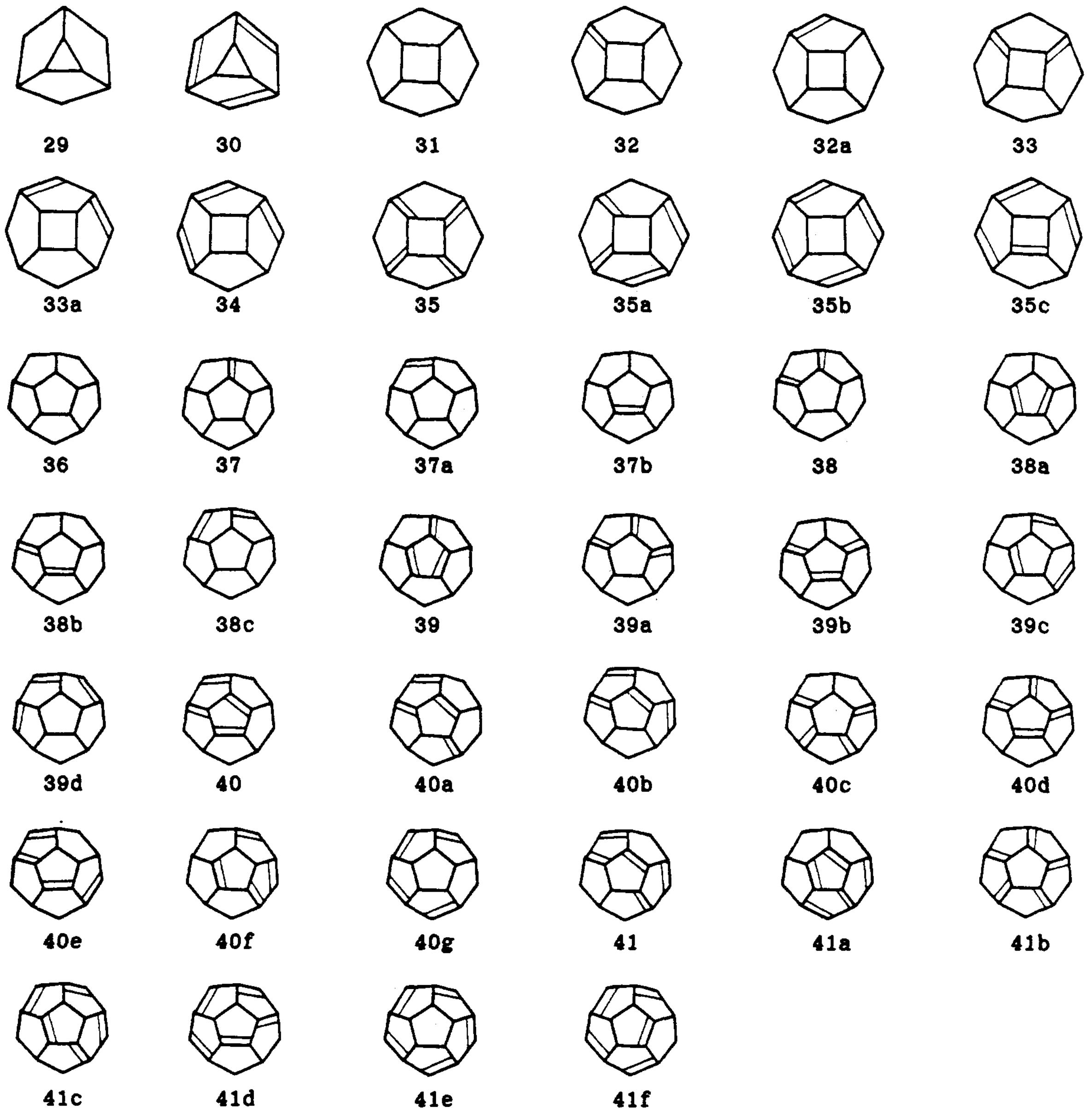
Figure 3. New structures investigated calculationally for possible trishomoaromatic character.

Table I. MMP2 Results for 8–12 and 24–28 (Energies in kcal/mol, Distances in Å)

				BO_{SCF}[a,b]		distance between sp^2 atoms[b]	
	method	ΔH_f	strain energy	1–2	2–x	1–2	2–x
8	MMP2	44.49	9.81	1.000		1.344	2.472
	MMP2(NBI)[c]	44.69	11.45	0.990	0.103	1.345 (1.34)[d,e]	2.457 (2.46)[d,e]
9	MMP2	61.45	19.30	1.000		1.357	2.494
	MMP2(NBI)	60.17	19.32	0.993	0.087	1.338 (1.319)[e,f]	2.494 (2.533)[e,f]
10	MMP2	75.12	47.72	1.000		1.336	2.807
	MMP2(NBI)	74.70	47.74	0.992	0.092	1.337 (1.323)[g]	2.807 (2.848)[g]
11	MMP2	36.24	18.83	1.000		1.343	2.913
	MMP2(NBI)	35.94	18.80	0.994	0.077	1.343	2.913
12	MMP2	45.44	54.17	1.000		1.349	2.605
	MMP2(NBI)	47.37	56.94	0.984	0.134	1.351	2.578 (2.60)[h]
24	MMP2	131.89	106.11	1.000		1.356	2.074
	MMP2(NBI)	130.23	109.84	0.959	0.219	1.362	2.068
25	MMP2	157.20	124.01	1.000		1.362	2.103
	MMP2(NBI)	155.18	126.77	0.967	0.196	1.368	2.101
26	MMP2	91.26	72.76	1.000		1.347	2.319
	MMP2(NBI)	91.38	72.25	0.980	0.151	1.350	2.310
27	MMP2	69.88	61.35	1.000		1.353	2.271
	MMP2(NBI)	69.46	63.70	0.975	0.168	1.356	2.256
28	MMP2	23.61	66.92	1.000		1.357	2.950
	MMP2(NBI)	24.42	67.89	0.993	0.089	1.358	2.952

[a] Bond order between sp^2 atoms as given by the MMP2 SCF cycle. [b] Homoconjugated sp^2 atoms are designated by x (i.e., 2–4 in 2 and 2–5 in 3). [c] MMP2 including nonbonding pp interactions (NBI) in the SCF cycle (i.e., homoconjugation present). [d] X-ray data.[9b] [e] Values from MINDO/3 calculations are 1.344 and 2.573 Å for 1, and 1.349 and 2.637 Å for 2.[8b] [f] X-ray data.[10a] [g] X-ray data.[11] [h] X-ray data.[13]

the decreased distance between the homoconjugated double bonds, contribute to the increase in strain energy. Although repulsive hydrogen–hydrogen interactions are not present in 12, ring closure (the extreme result of overlap) would lead to three pairs of fused four-membered rings.



29 30 31 32 32a 33

33a 34 35 35a 35b 35c

36 37 37a 37b 38 38a

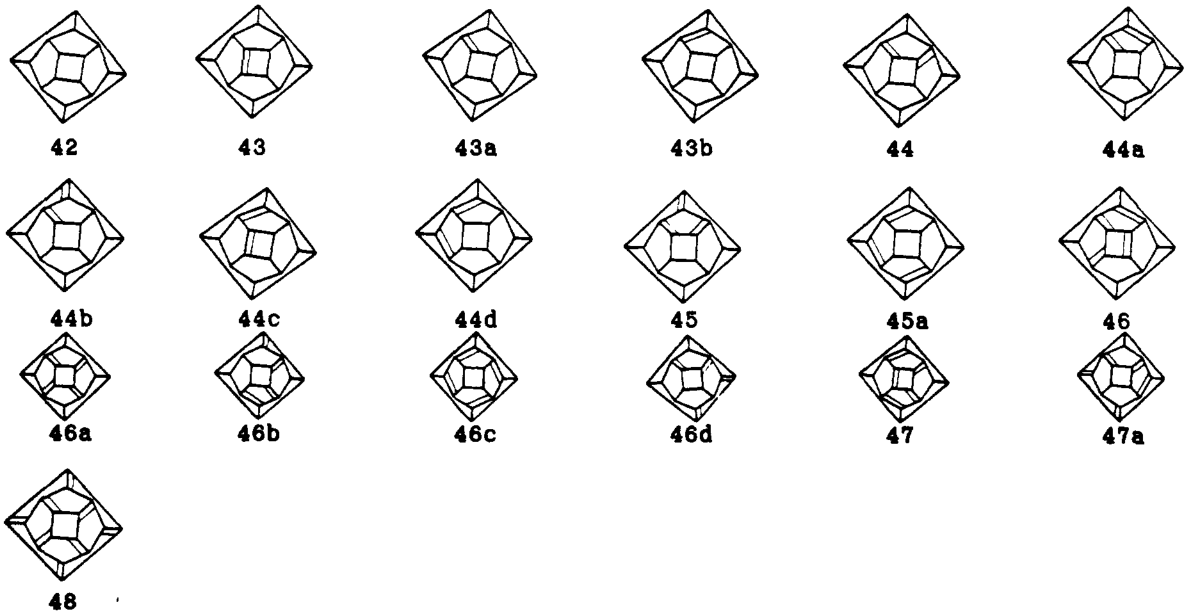
38b 38c 39 39a 39b 39c

39d 40 40a 40b 40c 40d

40e 40f 40g 41 41a 41b

41c 41d 41e 41f

Figure 4. [*n*]Peristylapolyenes investigated.



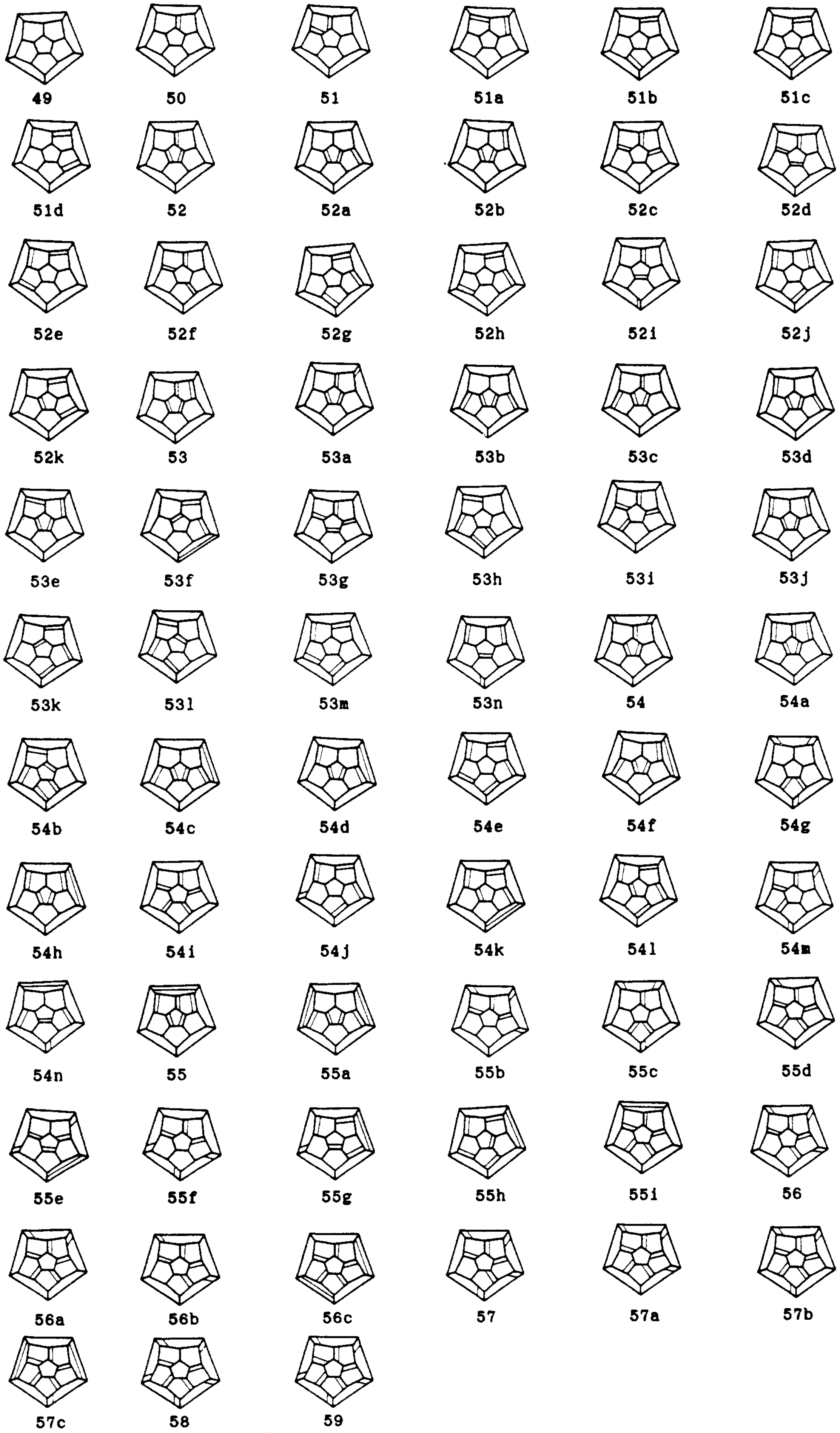
42 43 43a 43b 44 44a

44b 44c 44d 45 45a 46

46a 46b 46c 46d 47 47a

48

Figure 5. *p*-[$4^2.5^8$]Hexadecahedrapolyenes investigated.



49 **50** **51** **51a** **51b** **51c**

51d **52** **52a** **52b** **52c** **52d**

52e **52f** **52g** **52h** **52i** **52j**

52k **53** **53a** **53b** **53c** **53d**

53e **53f** **53g** **53h** **53i** **53j**

53k **53l** **53m** **53n** **54** **54a**

54b **54c** **54d** **54e** **54f** **54g**

54h **54i** **54j** **54k** **54l** **54m**

54n **55** **55a** **55b** **55c** **55d**

55e **55f** **55g** **55h** **55i** **56**

56a **56b** **56c** **57** **57a** **57b**

57c **58** **59**

Figure 6. Dodecahedrapolyenes investigated.

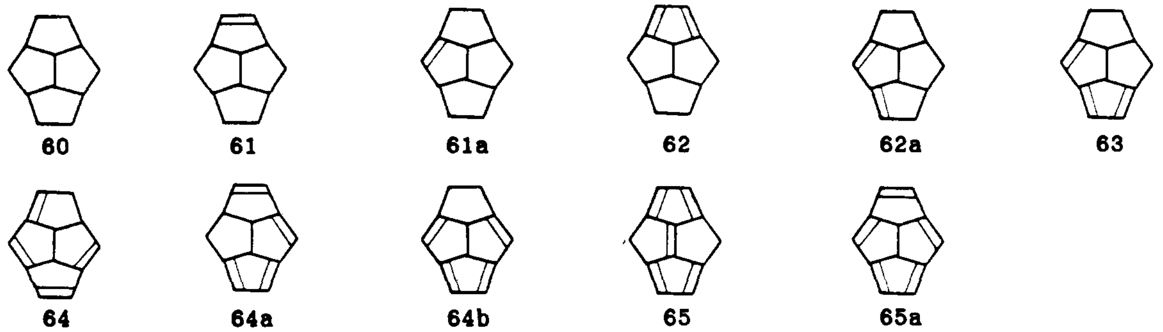


Figure 7. Tetraquinapolyenes investigated.

Table II. Energetic Effects of Homoconjugation in 8-12 and 24-28

		change in stability (kcal/mol)^b			band split (eV)	
	β^a	$\Delta\Delta H_f$	ΔE_{el}	Δ strain energy	calcd	exptl
8	0.319	0.20	-1.46	1.64	1.05	[0.9]^c
9	0.278	-1.28	-1.30	0.02	0.92	[0.35]^d
10	0.307	-0.42	-0.43	0.02	0.99	[0.47]^e
11	0.262	-0.28	-0.28	-0.03	0.86	
12	0.400	1.93	-0.88	2.77	1.30	[0.3]^f
24	0.527	-1.66	-5.41	3.73	1.75	
25	0.482	-2.02	-4.78	2.76	1.61	
26	0.427	0.12	-2.39	2.49	1.40	
27	0.466	-0.42	-2.80	2.35	1.48	
28	0.291	0.71	-0.17	0.97	0.94	

[a] Resonance integral between nonbonding sp^2 carbons. [b] Determined by: MMP2(NBI) value - MMP2 value. $\Delta\Delta H$ is the overall change in heats of formation; ΔE_{el} is the stabilization due to unconjugated overlap as given by the MMP2 program; and Δ strain energy is the change (usually increase) in strain energy. [c] Reference 9c. [d] Reference 10b. [e] Reference 11b. [f] Reference 13.

In this set only **8** and **11** are nonrigid structures. Previous calculations of the crown geometry of **11**, which allows for maximum homoconjugation, showed that it was not even the most stable conformation.[12b] Our calculations support these conclusions; the helix conformation has a heat of formation 7.0 kcal/mol lower than that of the crown geometry. Since we were interested in homoconjugation, the crown conformation of **11** was examined. The low energy crown conformation of **8** also was studied.[8b]

The symmetric ($D_{3h} \rightarrow D_{6h}$) trimerzation of acetylene to benzene has a substantial activation barrier of 72.7 kcal/mol (MINDO/3) [62 kcal/mol (MP3/6-31G*)]; the transition structure ("state") occurs when the carbons forming the new bonds are about 2.2 Å apart.[14] However, after this barrier is passed, a large attractive potential develops. By analogy (as suggested by Houk and Paquette) one would expect homoaromaticity to be present when the distance between the homoconjugating atoms is 2.2 Å or less. The distance between the double bonds in compounds **8**–**12** prevents trishomoaromaticity, since the homoconjugating carbons are all more than 2.4 Å apart (Table I). This is in the repulsive part of the potential energy surface, explaining why homoaromatic interactions have appeared to be destabilizing.[11a,14]

We explored several new systems (Figure 3) for trishomoaromaticity calculationally. By placing bridging methylene groups between the homoconjugating carbons in **8**–**11**, the repulsive hydrogen–hydrogen interactions are removed, the double bonds are forced together (Table I), and the π MOs are aligned into the plane defined by the double-bond carbon atoms. Thus, overlap is facilitated. As expected, increased electronic stabilization (ΔE_{el} = -2.4 to -5.4 kcal/mol) is observed in compounds **24**–**27** (compared to **8**–**11**) when homoconjugative interactions are included. However, these favorable effects are still quite small and are overridden by concurrent increases in strains energies (Δ strain energy = 2.4–3.7 kcal/mol, Table II). In an attempt to reduce the increase in strain due to angle deformation (which, in the extreme, would lead to the formation of three-membered rings), a molecule with three-carbon (-$CH_2CH_2CH_2$-) bridges (**28**) was studied. When the homoconjugation interaction is "turned on" a smaller increase in strain energy results (1.0 kcal/mol). However, due to the greater distance between the homoconjugating atoms (3.0 Å), electron delocalization is less, and there is no significant (0.7 kcal/mol) stabilization due to trishomoconjugation.

Separating the p AOs from the σ framework allows direct evaluation of the effect of homoconjugation on splitting the orbital energies.[9–11,13] The MMP2 calculated MO eigenvalues are due to interactions between the p AOs and are not complicated by hyperconjugation. For this reason, agreement with experimental values is not very good (Table II). Compounds with more extensive σ skeletons tend to have larger hyperconjugative interactions with the π MOs. Thus, the experimental values are considerably smaller than those calculated by MMP2 (Table II).

In summary, it is easy to understand why extensive in-plane trishomoaromaticity has not been found in the known trienes (**8**–**13**).[8–14] The very modest electronic stabilization due to delocalization cannot be enhanced by changes in geometry as this increases the σ skeleton strain energy (Table II). For trishomoconjugation to be effective, two conditions must be met: the σ framework must be conducive to homoconjugation, and the π units should be substantially less than 2.2 Å apart. This will not be easy to achieve. For example, the new hydrocarbons (**24**–**28**) do *not* appear to be promising candidates for the realization of neutral trishomoaromaticity.

B. In-Plane and Radial Aromaticity. Double bonds were introduced (calculationally) into the [n]peristylanes (n = 3–5) p-[4^2.5^8]hexadecahedrane, dodecahedrane, and tetraquinacane polycyclic frameworks (Figure 2) in order to probe the effects of in-plane and radial conjugation. Not all possible polyene isomers were investigated, only those with salient features of interest. Representations of the olefins as planar graphs are shown in Figures 4–7. Figure 2 is useful for visualizing these systems in three dimensions.

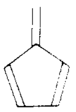
As indicated by the calculated heats of formation (Tables III–VI), isomers with conjugated double bonds are more stable. This is especially true for polyenes with extended conjugation, in particular those containing fulvene, pentalene, fulvalene, or acepentylene part structures. For example, the two most stable dodecahedrapentaene isomers (**54** and **54a**) contain fulvalene and acepentylene moieties, respectively. Cyclic conjugation of

Table III. MMP2 Calculated Energies (kcal/mol) for [*n*]Peristylapolyenes (Figure 4)

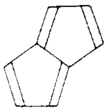
[*n*]	molecule[a]	no. DB[b]	ΔH_f	relΔH_f[c]	strain energy	BE_{SCF}[d]
3	**29**	0	22.93	0	52.11	
	30 (cy)	3	188.77	0	150.48	−696.95
4	**31**	0	13.87	0	54.17	
	32	1	39.42	0	55.49	−129.05
	32a	1	45.16	5.74	59.32	−129.33
	33 (c)	2	57.74	0	51.98	−357.37
	33a (c)	2	84.95	27.21	75.33	−357.04
	34 (c)	3	114.94	0	81.56	−584.65
	35 (rc)	4	101.96	0	54.15	−909.64
	35a (c)	4	126.46	24.50	74.98	−814.83
	35b (cy)	4	153.73	51.77	95.70	−907.25
	35c (c)	4	157.46	55.50	102.32	−812.99
5	**36**	0	−5.56	0	45.41	
	37	1	17.15	0	43.87	−129.35
	37a	1	18.43	1.28	43.25	−129.37
	37b	1	20.61	3.46	47.35	−129.25
	38 (rc)	2	34.44	0	39.11	−358.05
	38a (c)	2	39.45	5.01	44.07	−357.94
	38b	2	42.01	7.57	45.52	−356.84
	38c (c)	2	44.42	9.98	45.12	−356.98
	39	3	52.99	0	37.53	−685.29
	39a	3	58.10	5.11	40.87	−586.20
	39b (c)	3	61.66	8.67	42.57	−584.97
	39c	3	77.25	24.26	51.69	−387.94
	39d	3	78.75	25.76	56.14	−585.30
	40 (ext)	4	69.28	0	31.36	−1011.10
	40a (ext)	4	74.82	5.54	36.56	−914.15
	40b (ext)	4	79.54	10.26	39.33	−914.17
	40c (rc)	4	83.04	13.76	44.05	−814.44
	40d	4	86.13	16.85	48.10	−911.85
	40e (c)	4	89.30	20.02	46.10	−814.61
	40f (c)	4	92.20	22.92	50.07	−814.39
	40g (c)	4	101.68	32.40	55.56	−813.45
	41 (ext)	5	87.01	0	28.17	−1241.86
	41a (ext)	5	91.05	4.04	28.57	−1334.01
	41b (rc)	5	101.35	14.34	43.21	−1141.14
	41c (cy)	5	109.85	22.84	51.09	−1146.83
	41d (c)	5	118.80	31.79	49.19	−1041.73
	41e (cy)	5	124.66	37.65	62.79	−1145.36
	41f (c)	5	125.16	38.15	56.53	−1041.60

[a] The relationship of the double bonds is given in parentheses in this and the following tables: c = conjugated; cy = cyclic conjugated (These are of particular interest as they may exhibit "aromaticity" or "antiaromaticity".); rc = radially conjugated; ext = extended conjugation; all = all carbons are "sp^2" hybridized. [b] Number of double bonds present. [c] The relative ΔH_f for molecules with similar number of double bonds. [d] Bond energy from SCF calculation on p AOs as given by the MMP2 program.

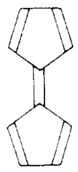
the polyenes usually is associated with lower heats of formation (compared to noncyclic conjugation); however, σ skeleton strain may oppose such arrangements. Noncyclic conjugated polyenes prefer the s-cis to the trans configuration as is the case with planar acyclic polyenes.[28] For example, the s-cis configuration of the double bonds in dodecahedratetraene (**53b**) is 12.6 kcal/mol lower in energy than the all-trans arrangement in **53m**.



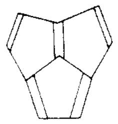
fulvene



pentalene



fulvalene



acepentylene

Table IV. MMP2 Calculated Energies (kcal/mol) for *p*-[$4^2.5^8$]Hexadecahedrapolyenes (Figure 5)[a]

molecule	no. DB	ΔH_f	relΔH_f	strain energy	BE_{SCF}
42	0	54.35	0	91.29	
43	1	80.93	0	93.66	−128.78
43a	1	81.04	0.11	93.75	−129.03
43b	1	83.11	2.18	95.82	−129.22
44 (c)	2	100.46	0	91.26	−357.31
44a (c)	2	102.40	1.94	92.89	−357.51
44b (c)	2	104.85	4.39	94.17	−356.18
44c	2	105.46	5.00	95.06	−356.16
44d (c)	2	110.00	9.54	99.69	−356.66
45 (ext)	3	118.06	0	88.17	−684.02
45a (c)	3	137.99	19.93	105.34	−584.64
46 (ext)	4	138.00	0	87.05	−1008.38
46a (rc)	4	146.31	8.31	94.87	−909.64
46b (c)	4	150.54	12.54	97.14	−813.98
46c (cy)	4	165.67	27.67	108.32	−907.09
46d (c)	4	182.95	44.95	123.32	−784.87
47 (ext)	5	150.76	0	84.44	−1340.23
47a (cy)	5	159.92	9.16	92.11	−1146.36
48 (all)	8	204.05	0	64.82	−2594.01

[a] See Table III for definition of terms.

In-plane and radial p AO delocalization is evaluated by inspecting the alternating conjugated compounds (**30**, **35**, **35b**, **41c**, **41e**, **46a**, **46c**, **47a**, **54b**, **54e**, **55a**, **55e**, **65a**) and the corresponding nonalternating compounds (**39**, **40**, **40d**, **41**, **41a**, **41b**, **45**, **47**, **48**, **52**, **53**, **53g**, **54a**, **54i**, **55**, **59**, and **65**). The first group includes potentially aromatic ($4n + 2$) and antiaromatic ($4n$) cyclic conjugated p systems. The nonalternating conjugated systems investigated varied widely and had 6–20 p electrons. The following discussion will employ several criteria to assess the degree of aromaticity in these compounds.

Heats of hydrogenation often have been used to evaluate aromaticity.[29] However, the serious drawbacks of this method have been pointed out. Several factors determine heats of hydrogenation, and the underlying reason for an observed deviation from "standard values" can be obscured.[30] Changes in strain must be taken into account to evaluate the effect of π bond delocalization from heats of hydrogenation accurately. While it is difficult to assess the effect of strain on heats of hydrogenation experimentally, this can easily be done by empirical force field calculations. For example, the calculated heat of hydrogenation of the first double bond in benzene is 4.6 kcal/mol endothermic (MMP2); however, the strain increase accompanying this process is 4.4 kcal/mol.[31]

Table VII summarizes the changes in energies associated with the hydrogenation of four cyclic dodecahedrapolyenes and shows the effect strain has on the heats of hydrogenation. The difference between the heats of formation calculated for the olefinic and saturated systems is ΔH_{hyd}. The differences in strain energies (Δstrain energy)[32] as given by the MMP2 program is then subtracted to give the "strainless heat of hydrogenation" ($\Delta H_{shy.}$) defined as $\Delta H_{shy.} = \Delta H_{hyd} - \Delta$strain energy. The $\Delta H_{shy.}$ values more accurately reflect the effect conjugation has on stabilizing the hydrogenated double bond. In a few cases, this is quite significant.

The ten electron systems with cyclic conjugation, **54b** and **54e**, have significantly smaller heats of hydrogenation than their isomers with noncyclic conjugation, e.g., **54h** and

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[31] McEwen, A. B., unpublished results.

[32] This is analogous to "olefin strain", defined by: Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

Table V. MMP2 Calculated Energies (kcal/mol) for Dodecahedrapolyenes (Figure 6)[a]

molecule	no. DB	ΔH_f	relΔH_f	strain energy	BE_{SCF}
49	0	22.17[b]	0	68.94	
50	1	47.39 [64.81][c]	0	69.92 [87.87]	−129.30
51 (rc)	2	64.59	0	64.97	−357.95
51a (c)	2	69.27	4.68	68.59	−356.87
51b	2	72.61	8.02	70.91	−258.61
51c	2	73.33	8.74	71.63	−258.60
51d	2	73.89	9.30	72.19	−258.59
52 (ext)	3	79.37	0	59.42	−685.05
52a (c)	3	82.59	3.22	61.30	−587.05
52b (c)	3	87.25	7.88	65.00	−586.07
52c (rc)	3	88.81	9.44	67.25	−586.08
52d (rc)	3	90.71	11.34	68.23	−585.08
52e (c)	3	90.82 (90.62)[d]	11.45	67.42 (67.27)	−584.92 (−584.95)
52f	3	91.47	12.10	67.64	−487.21
52g	3	95.89	16.52	70.96	−486.12
52h	3	96.05 (96.06)	16.68	71.12 (71.17)	−486.14 (−486.17)
52i	3	98.32 (97.76)	18.95	72.39 (72.47)	−387.80 (−388.45)
52j	3	101.16	21.79	75.22	−387.85
52k	3	101.70 (101.48)	22.33	75.77 (77.08)	−387.83
53	4	91.25	0	49.92	−1011.10
53a	4	97.95	6.70	56.10	−913.89
53b (c)	4	100.51 (100.49)	9.26	57.65 (57.65)	−816.25 (−816.26)
53c (c)	4	104.57	13.32	63.12	−913.59
53d (c)	4	105.85 (104.94)	14.60	62.05 (61.67)	−815.25 (−815.77)
53e (c)	4	106.46 (106.23)	15.21	61.76 (61.41)	−814.33 (−814.21)
53f (c)	4	107.77	16.52	61.98	−813.21
53g (rc)	4	108.14 (107.72)	16.89	65.62 (65.38)	−911.73 (−911.91)
53h (c)	4	109.45	18.20	64.64	−814.25
53i (rc)	4	110.85	19.60	67.40	−814.22
53j (c)	4	111.04	19.79	66.35	−814.30
53k (rc)	4	112.15	20.90	66.29	−813.11
53l (c)	4	112.21	20.96	66.32	−813.07
53m (c)	4	113.11 (113.03)	21.86	67.18 (67.08)	−813.12 (−813.11)
53n (uc)	4	131.29 (130.76)	40.04	81.12 (82.28)	−517.00 (−518.69)
54 (ext)	5	106.41 (107.26)	0	44.61 (45.09)	−1241.30 (−1241.37)
54a (ext)	5	112.79 (112.48)	6.38	47.84 (47.64)	−1334.15 (−1334.25)
54b (cy)	5	119.98 (119.96)	13.57	60.00 (60.10)	−1146.95 (−1146.82)
54c (c)	5	120.54	14.13	56.13	−1045.41
54d (c)	5	125.08	18.67	59.73	−1044.43
54e (cy)	5	125.67 (123.32)	19.26	63.70 (62.31)	−1145.01 (−1145.95)
54f (c)	5	125.84 (125.44)	19.43	60.63 (60.39)	−1044.51 (−1044.66)
54g (rc)	5	127.87	21.46	61.50	−1042.78
54h (c)	5	129.30 (129.80)	22.89	63.22 (63.59)	−1043.61 (−1043.49)
54i (rc)	5	130.34 (130.26)	23.93	67.54 (67.56)	−1140.84 (−1140.94)
54j (c)	5	131.83	25.42	64.50	−1042.38
54k (c)	5	134.17 (133.11)	27.76	65.87 (65.45)	−1041.27 (−1041.91)
54l (c)	5	134.50 (134.36)	28.09	66.12 (67.24)	−1041.25 (−1042.53)
54m (rc)	5	135.86 (135.82)	29.45	68.83 (68.82)	−1042.08 (−1042.10)
54n	5	149.14	42.73	74.76	−646.13
55	5	129.05 (132.20)	0	46.30 (45.55)	−1662.97 (−1659.11)
55a (cy)	6	130.76 (130.76)	1.71	46.79 (46.79)	−1373.78 (−1373.79)
55b (ext)	6	135.30	6.25	46.10	−1656.51
55c (rc)	6	144.40	15.35	57.94	−1370.02
55d (rc)	6	147.20	18.15	64.78	−1468.62
55e (cy)	6	147.34 (141.52)	18.29	57.69 (55.91)	−1367.74 (−1371.96)
55f (rc)	6	152.25	23.20	66.68	−1370.79
55g (c)	6	152.92 (152.90)	23.87	63.31 (63.29)	−1270.65 (−1270.66)
55h (c)	6	157.98	28.93	67.12	−1269.31
55i (rc)	6	159.41	30.36	72.24	−1269.96
56 (ext)	7	145.56	0	42.32	−1989.11
56a (rc)	7	156.89	11.33	51.25	−1889.38
56b (rc)	7	165.61	20.05	63.40	−1796.16
56c	7	179.46	33.90	70.07	−1498.52
57 (ext)	8	162.30	0	40.47	−2317.05
57a (rc)	8	163.91	1.61	45.51	−2319.89
57b (rc)	8	175.43 (174.74)	13.13	50.24 (49.84)	−2217.16 (−2217.45)
57c (rc)	8	176.46	14.16	52.95	−2025.72
58 (ext)	9	170.07	0	37.29	−2748.72
59 (all)	10	175.73	0	23.55	−3268.03

[a] See Table III for definition of terms. [b] Previous values are 62.3 kcal/mol (MINDO/3) (Schulman, J. M.; Ditch, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 5677) and 22.5 kcal/mol (MM2) (Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127). [c] MM2 value. [d] Values in parentheses are from calculations including nonbonding pp interactions in the MMP2 SCF cycle.

54k (Table VII). The $\Delta H_{\mathrm{shy.}}$ values are somewhat more exothermic than ΔH_{hyd} for **54b** and **54e**, due to the increase in strain upon hydrogenation. The $\Delta H_{\mathrm{shy.}}$ for the first hydrogenation of **54b** is 6.1 kcal/mol less than that for **54h**, and that of **54e** is 6.3 kcal/mol less than that for **54k**. The enhanced stability of the 10-electron cyclic conjugated

Table VI. MMP2 Calculated Energies (kcal/mol) for Tetraquinapolyenes (Figure 7)[a]

molecule	no. DB	ΔH_f	relΔH_f	strain energy	BE_{SCF}
60	0	-17.61	0	29.28	
61	1	9.93	0	28.78	-129.37
61a	1	11.57	1.64	32.30	-129.35
62 (c)	2	33.92	0	32.90	-358.19
62 (c)	2	36.79	2.87	33.36	-356.91
63 (c)	3	61.57	0	37.01	-586.29
64 (c)	4	87.09	0	34.75	-813.25
64a (c)	4	91.08	3.99	41.22	-814.63
64b (c)	4	93.09	6.00	45.24	-814.60
65 (ext)	5	85.14	0	20.44	-1241.80
65a (cy)	5	106.62	21.48	41.34	-1146.90

[a] See Table III for definition of terms.

Table VII. Hydrogenation Effects of Selected Dodecahedrapolyenes (kcal/mol)

hydrogenation process			ΔH_{hyd}	Δstrain energy	$\Delta H_{shy.}$[a]
		A. Starting with 10-Electron Systems			
1)	cyclic	**54b** → **53h**	-10.53	4.64	-15.17
	linear	**54h** → **53h**	-19.85	1.42	-21.27
		53h → **52b**	-23.79	0.36	-24.15
		52b → **51**	-22.66	-0.03	-22.63
		51 → **50**	-17.20	4.95	-22.15
		50 → **49**	-25.22	-0.98	-24.24
2)	cyclic	**54e** → **53m**	-12.56	3.48	-16.04
	linear	**54k** → **53m**	-21.06	1.31	-22.37
		53m → **52e**	-22.29	0.24	-22.53
		52e → **51a**	-21.55	1.17	-22.72
		51a → **50**	-21.88	1.33	-22.21
		B. Starting with 12-Electron Systems			
1)	cyclic	**55a** → **54c**	-10.23	9.34	-19.57
	linear	**54c** → **53b**	-20.03	1.52	-20.52
		53b → **52a**	-17.92	3.65	-21.57
		52a → **51**	-18.00	3.67	-21.67
2)	cyclic	**55e** → **54f**	-21.50	2.94	-24.44
	linear	**54f** → **53d**	-19.99	1.42	-21.41

[a] Strainless heat of hydrogenation defined as: $\Delta H_{shy.} = \Delta H_{hyd} - \Delta$strain energy.

compounds also is indicated by the fact that the further hydrogenations leading in a stepwise manner to the completely saturated dodecahedrane all are more exothermic. In contrast, the potentially antiaromatic conjugated 12-electron systems, **55a** and **55e**, have $\Delta H_{shy.}$ differences compared to the linear analogues (**54c** and **54f**) of only −1.0 and +3.0 kcal/mol, respectively (Table VII). While the small ΔH_{hyd} for **55a** suggests strong stabilization, this is due to the large increase of strain on hydrogenation. This aromatic/antiaromatic pattern shown by the ΔH_{shy} criterion also is found in other cyclic polyenes where the eight-electron systems (**35b** and **46c**) are destabilized, and the ten-electron systems (**41c**, **41e**, **47a**, and **65a**) are stabilized (Table VIII). The nonalternating systems show little deviation in their $\Delta H_{shy.}$ values, all of which lie in the nonaromatic range (Table VIII).

The resonance integral (β) obtained from the SCF calculations on the p AOs reveals the extent of electron delocalization between conjugated atoms (Table VIII). The degree of "aromaticity" can be assessed by the differences in the extent of p electron delocalization. The resonance integral (β) for the C_1–C_2 and C_2–C_3 bonds in the cyclic conjugated ten-electron systems, **47a** and **54b**, are 0.845 vs. 0.783 (difference, $\Delta\beta = 0.062$) and 0.876 vs. 0.824 (difference, $\Delta\beta = 0.052$), respectively. These small $\Delta\beta$ values indicate diminished bond alternation, and suggest some aromatic character. In contrast, the 12-electron systems, **55a** and **55e**, have less delocalization ($\Delta\beta = 0.145$). The greater bond delocalization observed in the 10-electron systems (**47a** and **54b**) compared to the 12-electron systems (**55a** and **55e**) agrees with expectations based on the $4n + 2$ rule. Howver, the other cyclic polyenes do not show the same behavior. The 6-electron system **30** has a resonance integral difference of $\Delta\beta = 0.170$ which is larger than the difference in the 8-electron system **35b** ($\Delta\beta = 0.133$). In addition, the two 10-electron systems, **41c** and **65a**, exhibit substantial bond alteration, with $\Delta\beta = 0.203$ and $\Delta\beta = 0.231$, respectively. These deviations probably are due to constraints imposed by the σ framework. The nonalternating hydrocarbons have $\Delta\beta$ values ranging from 0.091 to 0.177. Therefore, although the resonance integral difference criterium does indicate an increase in electron delocalization for some $4n + 2$ systems, there are several anomalies.

The resonance energy (RE) due to electron delocalization is also a measure of aromaticity.[33] Dewar's definition,[33e] $RE = E - E_{ref}$, is readily applicable to our systems; we can standardize our reference energies internally by using values for noncyclic polyenes. We define E as the MMP2 calculated bonding energy due to the p AOs (BE_{scf}) in a cyclic conjugated system, and E_{ref} as the calculated value for the hypothetical reference system using group increments and assuming additivity. We derived these group increments by using the noncyclic conjugated polyenes for the same polycyclic system. A positive RE value represents added stability due to favorable electronic interaction. In addition, RE per electron (REPE) also are given in Table VIII.

The calculated RE values for the cyclic conjugated alternating hydrocarbons are in accord with expectations based on the $(4n + 2)$ electron aromaticity rule. The 6- and 10-electron systems show slight to moderate stability due to cyclic conjugation (RE = 4.8 to 14.8) and, except for **55a** (RE = 1.9), the 8- and 12-electron systems are slightly destabilized (RE = −2.0 to −4.0, Table VIII). Most of the nonalternant systems can be classified as nonaromatic, because of their small absolute RE values.

"Aromaticity" may be assessed from the smallest bond order (BO) present in a cyclic conjugated system.[34] Jug has found that aromatic molecules have minimum BO values greater than 1.33 and antiaromatic compounds less than 1.21. The BO values reported here are termed "BO_{scf}", because they only apply to the pp conjugated system as determined from the MMP2 SCF calculations. Since CC bonds in the σ skeleton should have bond orders of 1.0, the total bond order for comparison with Jug's data should be $1.0 + BO_{scf}$. However, this is not quite the case. The BO_{scf} value we obtain for benzene is 0.667. The corresponding bond order of 1.667 differs from Jug's value of 1.751. For cyclobutadiene we obtain a single bond order of 1.000 as compared to Jug's 0.980. While direct application of Jug's criteria is not possible, the quantitative differences observed within our method appear to be significant.

The BO_{scf} values for the 6- and 10-electron systems reveal that these can be classified as weakly aromatic species, while the 8- and 12-electron systems are nonaromatic (Table VIII). The largest BO_{scf} value (0.561) is observed

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(33) (a) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722. Herndon, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 2404. Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 2413. (b) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750. (c) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305. (d) Hess, B. A., Jr.; Schaad, L. J. *J. Org. Chem.* **1971**, *36*, 3418. (e) Dewar, M. J. S.; De Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789. Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969. (f) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500. (g) Trinajstic, N.; Milun, M.; Gutman, I. *J. Am. Chem. Soc.* **1977**, *99*, 1692.

(34) Jug, K. *J. Org. Chem.* **1983**, *48*, 1344.

Table VIII. Criteria Used for Evaluating Aromaticity in the Alternating and Nonalternating Hydrocarbons in Tables III–VI (kcal/mol)

molecule	no. elec[a]	ΔH_{shy}.[b]	β[c]	$\Delta\beta$[d]	RE[e]	REPE[f]	BO_{SCF}[g]
			A. Alternating Hydrocarbons				
30	6		0.937, 0.767	0.170	14.84	2.473	0.378
35	8		0.909, 0.732	0.177	−3.64	−0.455	0.253
35b	8	−23.63	0.791, 0.658	0.133	−2.02	−0.259	0.232
46a	8		0.911, 0.735	0.176	−3.48	−0.435	0.252
46c	8	−24.70	0.865, 0.719	0.146	−3.75	−0.469	0.239
41c	10	−15.56	0.919, 0.716	0.203	8.06	0.806	0.361
41e	10	−15.75	0.861, 0.758	0.103	5.22	0.522	0.386
47a	10	−14.41	0.845, 0.783	0.062	4.75	0.475	0.561
54b	10	−15.17	0.876, 0.824	0.052	8.02	0.802	0.523
54e	10	−16.04	0.906, 0.793	0.113	8.10	0.810	0.420
65a	10	−12.94	0.952, 0.715	0.237	8.00	0.800	0.348
55a	12	−19.57	0.922, 0.777	0.145	1.88	0.157	0.312
55e	12	−24.44	0.920, 0.775	0.145	−4.36	−0.363	0.309
			B. Nonalternating Hydrocarbons				
39	6	−19.20	0.922, 0.757	0.165	1.92	0.320	0.277
45	6	−20.69	0.896, 0.744	0.152	−0.81	−0.135	0.270
52	6	−20.33	0.927, 0.773	0.154	0.21	0.035	0.278
40	8	−22.46	0.911, 0.762	0.149	0.88	0.110	0.259
40d	8	−20.80	0.928, 0.762	0.166	−0.63	−0.079	0.274
53	8	−21.38	0.924, 0.767	0.157	−1.63	−0.204	0.254
53g	8	−20.96	0.930, 0.772	0.158	−1.03	−0.129	0.278
41	10	−20.48	0.926, 0.769	0.157	4.13	0.413	0.288
41a	10	−19.15	0.919, 0.767	0.152	−2.36	−0.236	0.274
57	10		0.888, 0.729	0.159	1.50	0.450	0.204
54	10	−19.95	0.922, 0.772	0.150	0.63	0.063	0.277
54a	10	−22.51	0.932, 0.759	0.173	−6.30	−0.630	0.219
54i	10	−19.55	0.926, 0.772	0.154	−0.71	−0.071	0.276
55	12	−21.81	0.921, 0.770	0.151	−4.16	−0.347	0.249
48	16		0.834, 0.743	0.091	−26.23	−1.639	0.186
59	20	−19.38	0.897, 0.771	0.126	−1.17	−0.058	0.192

[a] Number of p electrons. [b] Strainless heat of hydrogenation. [c] Largest and smallest resonance integrals (β) as calculated by the MMP2 SCF cycle. [d] Difference in these resonance integrals. [e] Resonance energy (RE) of conjugated system (see text). [f] RE per electron (REPE). [g] The smallest pp bond order as determined by the MMP2 SCF cycle. [h] Hydrogenation products were uncalculable due to program limitations.

Table IX. MNDO Heats of Formation (kcal/mol) for 54e

compd	ΔH_f	$\text{CI}\Delta H_f$[a]	orbital energies (eV)[b]
54e (non equiv 1)[c]	332.79	329.36	−8.5, −8.5, −10.5, −10.5, −11.7
(equiv 2)	335.19	328.80	−8.2, −8.2, −10.6, −10.6, −11.8

[a] Calculation utilizing 1SCF cycle with singlet CI on the closed shell (RHF) optimized geometry. [b] Energies of the MOs resulting from predominantly the p AOs. [c] Structure with nonequivalent (nonequiv) or equivalent (equiv) bond lengths in the cyclic conjugated system.

for compound **47a**. This value suggests significant aromatic character to be present (compared to 0.667 obtained for benzene). Moreover, **35b** with eight electrons has a much lower value ($\text{BO}_{\text{scf}} = 0.232$). This is in the range of the nonalternating systems ($\text{BO}_{\text{scf}} = 0.186$ to 0.288) which may be classified as nonaromatic.

Two geometries of the cyclic ten-electron dodecahedrapentene, **54e**, were calculated by using the semiempirical MNDO program[27] (Table IX); these had equivalent and alternating bond lengths between sp^2 carbons (Figure 8). In cyclic conjugated systems electron correlation effects favor structures with equivalent bond lengths.[35] Therefore, in addition to calculations using closed shell (RHF) optimized geometries, one SCF cycle with singlet configurational interaction (MNDO-CI) was carried out on the RHF geometries.[36]

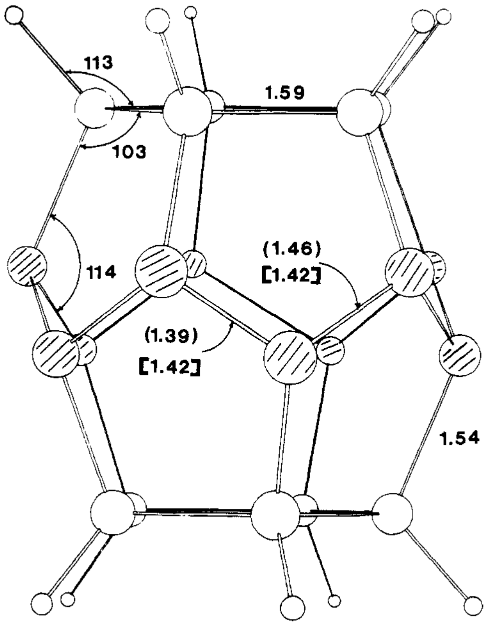

Figure 8. MNDO geometry of **54e** (bond lengths in Å, angles in degrees). Parameters for structure [1] are in parentheses and for structure [2] are in brackets (see Table IX). The sp^2 atoms are shaded.

At the MNDO-CI level, the structure with equal bond lengths is stabilized relative to the one with nonequivalent, alternating bond legnths. For **54e** at the closed shell optimized geometry the heat of formation obtained by using the nonequivalent geometry is 2.4 kcal/mol lower than the equivalent (Table IX). However, the structure with

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(36) The use of CI may overemphasize the energetic effects of electron correlation which MNDO has been paramaterized to include.

equivalent bond lengths is 0.6 kcal/mol more stable when CI is included. The MNDO calculated MOs resulting from the ten p AOs in **54e** are split energetically into a characteristic aromatic pattern, comprising one low energy and two sets of doubly degenerate bonding orbitals (Table IX).

In conclusion, in-plane and radial cyclic conjugation of p orbitals in hydrocarbons is predicted. The alternate cyclic radially conjugated 6- and 10-electron systems show aromaticity by all criteria employed (Table VIII). When corrected for strain effects, the stabilization energies due to radial ("in-plane") aromaticity often are 8 kcal/mol or so. In contrast, the 4*n*-electron systems, although otherwise similar in structure, show a destabilizing effect of small magnitudes. Although the nonalternate conjugated systems are stable isomers, they are nonaromatic.

Of additional interest are other large spherical unsaturated carbon molecules, several of which have been observed in the gas phase.[37] In particular, the truncated icosahedral C_{60} molecule has been predicted to have a large, stabilizing, delocalization energy.[38] An interesting $C_{20}H_{10}$ polyene, topologically similar to dodecahedrapentene (**54e**), has been suggested by Kornilov.[39]

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Registry No. 8, 696-86-6; **9**, 6053-74-3; **10**, 66081-13-8; **11**, 4736-48-5; **12**, 91266-48-7; **24**, 104374-23-4; **25**, 104374-24-5; **26**, 104374-25-6; **27**, 104374-26-7; **28**, 104374-27-8; **29**, 20454-87-9; **30**, 104374-28-9; **31**, 85850-64-2; **32**, 104374-29-0; **32a**, 104374-30-3; **33**, 104374-31-4; **33a**, 104374-32-5; **34**, 104374-33-6; **35**, 104374-34-7; **35a**, 104374-35-8; **35b**, 104374-36-9; **35c**, 104374-37-0; **36**, 63127-44-6; **37**, 104374-38-1; **37a**, 104374-39-2; **37b**, 104374-40-5; **38**, 104374-41-6; **38a**, 104374-42-7; **38b**, 104374-43-8; **38c**, 104374-44-9; **39**, 104374-45-0; **39a**, 104374-46-1; **39b**, 104374-47-2; **39c**, 104374-48-3; **39d**, 104374-49-4; **40**, 104374-50-7; **40a**, 104374-51-8; **40b**, 104374-52-9; **40c**, 104374-53-0; **40d**, 104374-54-1; **40e**, 104374-55-2; **40f**, 104374-56-3; **40g**, 104374-57-4; **41**, 104374-58-5; **41a**, 104374-59-6; **41b**, 104374-60-9; **41c**, 104374-61-0; **41e**, 104374-62-1; **41f**, 104374-63-2; **42**, 104374-64-3; **43**, 104374-65-4; **43a**, 104374-66-5; **43b**, 104374-67-6; **44**, 104374-68-7; **44a**, 104374-69-8; **44b**, 104374-70-1; **44c**, 104374-71-2; **44d**, 104374-72-3; **45**, 104374-73-4; **45a**, 104393-12-6; **46**, 104374-74-5; **46a**, 104374-75-6; **46b**, 104374-76-7; **46c**, 104374-77-8; **46d**, 104374-78-9; **47**, 104374-79-0; **47a**, 104374-80-3; **48**, 104374-81-4; **49**, 4493-23-6; **50**, 77159-24-1; **51**, 104374-82-5; **51a**, 104374-83-6; **51b**, 104374-84-7; **51c**, 104374-85-8; **51d**, 104374-86-9; **52**, 104374-87-0; **52a**, 104374-88-1; **52b**, 104374-89-2; **52c**, 104374-90-5; **52d**, 104374-91-6; **52e**, 104374-92-7; **52f**, 104374-93-8; **52g**, 104374-94-9; **52h**, 104374-95-0; **52i**, 104374-96-1; **52j**, 104374-97-2; **52k**, 104374-98-3; **53**, 104374-99-4; **53a**, 104375-00-0; **53b**, 104375-01-1; **53c**, 104375-02-2; **53d**, 104375-03-3; **53e**, 104375-04-4; **53f**, 104375-05-5; **53g**, 104375-06-6; **53h**, 104375-07-7; **53i**, 104375-08-8; **53j**, 104375-09-9; **53k**, 104375-10-2; **53m**, 104375-11-3; **53n**, 104375-12-4; **54**, 104375-13-5; **54a**, 104375-14-6; **54b**, 104375-15-7; **54c**, 104375-16-8; **54d**, 104375-17-9; **54e**, 104375-18-0; **54f**, 104375-19-1; **54g**, 104375-20-4; **54h**, 104375-21-5; **54i**, 104375-22-6; **54j**, 104375-23-7; **5jk**, 104375-24-8; **5jl**, 104375-25-9; **54m**, 104375-26-0; **54n**, 104375-27-1; **55**, 104375-28-2; **55a**, 104375-29-3; **55c**, 104375-30-6; **55d**, 104375-31-7; **55e**, 104375-32-8; **55f**, 104375-33-9; **55g**, 104375-34-0; **55h**, 104375-35-1; **55i**, 104375-36-2; **56**, 104375-37-3; **56a**, 104375-38-4; **56b**, 104375-39-5; **56c**, 104375-40-8; **57**, 53129-39-8; **57a**, 104375-41-9; **57b**, 104375-42-0; **57c**, 104375-43-1; **58**, 104375-44-2; **59**, 104375-45-3; **60**, 60606-97-5; **61**, 104375-46-4; **61a**, 104375-47-5; **62**, 104375-48-6; **62a**, 104375-49-7; **63**, 104375-50-0; **64**, 104375-51-1; **64a**, 104375-52-2; **64b**, 104375-53-3; **65**, 104375-54-4; **65a**, 104375-55-5.

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Facile Synthesis of Allylic Nitro Compounds by *N*,*N*-Dimethylethylenediamine-Catalyzed Condensation of Aliphatic and Alicyclic Ketones with Primary Nitroalkanes

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Aliphatic as well as alicyclic ketones condense with primary nitroalkanes in the presence of *N*,*N*-dimethylethylenediamine (**1**) to give allylic nitro compounds selectively in good to excellent yields without forming α-nitro olefins. Condensation of 2-alkanones and 2-methylcyclopentanone with nitromethane produces the products of thermodynamic control, while the product of kinetic control is obtained from 2-methylcyclohexanone. Propiophenone, an aromatic ketone, reacted with nitromethane in a way analogous to aliphatic ketones to give the corresponding allylic nitro product. A reaction mechanism to account for the exclusive formation of allylic nitro compounds is proposed. Some allylic nitro compounds thus obtained are converted into α,β-unsaturated aldehydes and ketones by treatment with sodium methoxide and then $TiCl_3$ in a buffered solution.

The use of allylic compounds for carbon–carbon bond formation and for functionality transformation has been the subject of considerable recent development. Allylic nitro compounds are particularly versatile intermediates in that they can react both as nucleophiles and electrophiles.[1-3] In addition, the nitro group is readily trans-

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