basicities in the gas phase and various solutions.

Polarizability attenuation factors (PAF)[27] are used to evaluate the overall substituent polarization effect on a particular system in various solvents relative to the gas phase. PAF is defined as $\rho_\alpha(\text{gas})/\rho_\alpha(\text{sol})$, where ρ_α is the sensitivity of a reaction to substituent charge-induced stabilization. The closer this ratio is to unity means that stabilization of the ion is increasingly gained inherently and not from the solvent. A value of unity has been attained for large, stable, dispersed ions in water and DMSO.[28] For the more localized ions, such as ammonium ions, this value is greater than unity as a result of stability gained from solvation. For primary alkylammonium ions in aqueous medium, which are solvated primarily by three hydrogen bonds to water, it was observed that the substituent polarizability effect (ρ_α) is essentially zero.[29] This implies that stabilization by solvation overwhelms any inherent charged-induced stability.

For tertiary ammonium ion, with only the availability of one hydrogen bond to the solvent, stabilization by the solvent is much less reduced when compared to primary alkylammonium ions. Thus, of the solvents studied, the PAF value of 4.2 (Table II) for AN suggests that, in this solvent, the substituents of dimethylammonium ion have the greatest ability to exert their effect in an inherent stabilization by the polarizability effect, whereas DMSO (PAF = 8.5) shows the least.

The difference in polarizability attenuation factors in various solvents can be explained in terms of the energy involved in charge-induced stabilization given by eq 7,

$$E = -\alpha q^2/2Dr^4 \qquad (7)$$

where D is the dielectric constant on the medium, r is the distance from charge, and q is the distance to the center of material of polarizability, α. The energy is directly proportional to the square of the charge; therefore, due to the changes of relative residual charge, which results primarily from differences in specific solvation in different solvents, the energy will be larger in solvents with low hydrogen bond acceptor ability and vice versa.

The possibility of changes in basicities due to steric effects can be ruled out since there is a poor correlation between $\Delta G°$ and steric substituent constants, E_s.[30] Also, if steric hindrance to protonation or strain of the ion were fully operational, then as the alkyl substituent gets bulkier the basicities should decrease, but instead, the reverse is observed in all cases of solvents studied.

Alkyl-substituted dimethylammonium ions are solvated primarily by hydrogen bonds to the ion from the solvent, which serve to disperse the charge on the ion into the solvent offering some degree of stability to the ion. The ion also gains stability inherently from substituents via charge-induced stabilization. However, this stabilization is dictated by the extent of solvation of the ion. Acetonitrile and water interact the least with the ion, which results in a smaller solvent attenuation factor when compared to DMSO for which the large factor shows a strong interaction.

Acknowledgment. I am grateful to Professor Robert W. Taft for his encouragement.

Registry No. NMe_3, 75-50-3; $EtNMe_2$, 598-56-1; $PrNMe_2$, 926-63-6; $BuNMe_2$, 927-62-8; *i*-$PrNMe_2$, 996-35-0; *sec*-$BuNMe_2$, 921-04-0; *t*-$BuNMe_2$, 918-02-5; c-$C_6H_{11}NMe_2$, 98-94-2; *t*-$C_5H_{11}NMe_2$, 57757-60-5.

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Columnar Homoconjugation

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Received August 26, 1987

Homoconjugative orbital interactions in "columnar" cyclic arrays of π bonds are analyzed through a simple perturbation approach and through ab initio calculations. These interactions lead to Hückel arrays of bonding and antibonding orbitals and should have a net destabilizing effect. Specific compounds (**1–3**) which engender columnar homoconjugation consist of n ($n \geq 3$) 1,4-cyclohexadiene units which are connected in a cyclic structure of D_{nh} symmetry. These have been previously referred to as "beltenes". Optimized geometries (STO-2G, RHF) are reported for compounds with n = 3–5. Single point 3-21G calculations have been performed at optimized geometries. The double bonds in these columnar structures are predicted to be significantly pyramidalized. Orbital interactions and estimates for the potential stability of columnar structures are discussed.

Introduction

The concept of homoconjugation has proved fundamental to our understanding of the electronic structure and energetics of neutral and charged organic molecules and transition states.[1] This reflects the recognition that formally nonconjugated portions of molecules can undergo physically and chemically significant interactions. Homoconjugation occurs either through direct "through-

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(1) For a comprehensive review, see: Martin, H. D.; Mayer, B. *Angew Chem., Int. Ed. Engl.* **1983**, *22*, 283.

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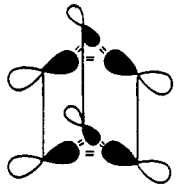
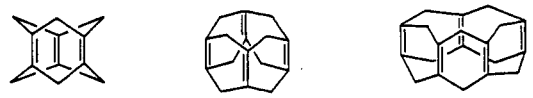


Figure 1. Topology for columnar homoconjugative interaction of three π bonds.

space" overlap or by "through bond" overlap[2] with a common atom; this often is studied by photoelectron spectroscopy.[1]

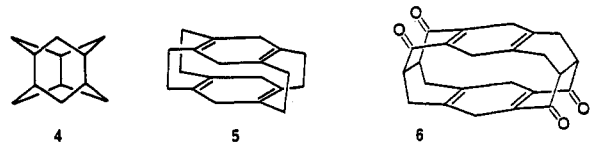
We consider here a type of interaction which we refer to as "columnar" homoconjugation.[3] The orbital topology is defined in Figure 1. This orbital array is of Hückel symmetry; i.e., there will always occur either zero or an even number of plus–minus orbital overlaps.[4] McEwen and Schleyer have described related systems as "in-plane homoaromatic".[5] We analyze here the homoconjugative interactions present in systems like Figure 1 and predict specific—as yet unknown—compounds in which these effects clearly should be manifested.

As archetypes for this columnar interaction, we suggest presently unknown polycyclics **1–3** and higher homologues. These are comprised of 1,4-cyclohexadiene units, with an overall D_{nh} molecular symmetry. Alder and Sessions have reported force-field calculations on **1–3** and homologues and refer to these as [*n*]beltenes.[6] We have referred to these structures as tri-, tetra-, and pentacolumnenes.[3] Interactions in **1–3** are of the 1,3-π–π variety.[1] These are formally polyhydroaromatics; interactions in linear analogues have been studied by photoelectron spectroscopy.[7]



1 **2** **3**

A few structures related to **1–3** are known. A hexahydro derivative of **1**, "iceane" (**4**), was reported some years ago.[8] Boekelheide and co-workers have reported the synthesis and orbital interactions in structure **5**.[9] This differs from



4 **5** **6**

1–3 due to its relatively strain-free nature and the dominance of hyperconjugative interactions, which result from π overlap with σ bonds of the ethano bridges. Interactions in **1–3** should be predominantly of the "through-space" variety.[2] McMurry and co-workers recently reported the synthesis of compounds which are related to **1–3** but in which the π bonds all lie in the same plane.[10] We have synthesized polyene **6**, which is related to hexacolumnene, but have been unable to study orbital interactions because this compound readily polymerizes.[11]

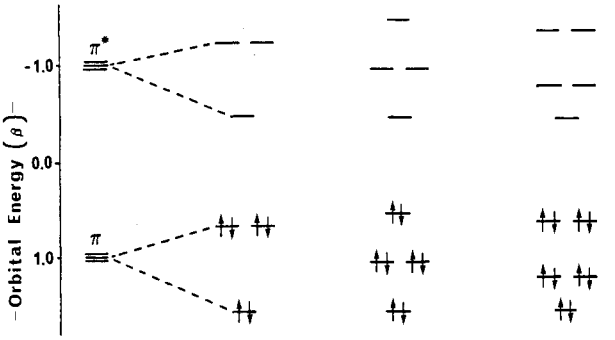


Figure 2. Hückel molecular orbital energies for interaction of three, four, and five double bonds.

It is important to note that double bonds in **1–3** should be substantially bent out of plane, or pyramidalized. Quite a number of structures with pyramidalized double bonds have been prepared either as stable structures or reactive intermediates.[12]

The present study has two goals. The first is to explore columnar homoconjugation at a purely theoretical level. The second is to estimate the potential isolability of polycyclics **1–3** and to predict some of their properties. Comparison between ab initio and MM2 results[6] is instructive.

Columnar Homoconjugation at the One-Electron Level

In its simplest form, "columnar" homoconjugation will be engendered by a series of n parallel double bonds, which overlap in a cyclic array (Figure 1) possessing D_{nh} symmetry. In this scheme, each double bond will have four 1,3-π–π interactions. Interaction of n double bonds in a columnar fashion should lead to n bonding and n antibonding molecular orbitals, with each group arranged as in the Hückel n carbon monocycle. Neglecting overlap, the pattern for three, four, or five double bonds should be as in Figure 2. Energies may simply be predicted by the usual Frost–Musulin mnemonic.[13] This requires basis energies of ± 1 (π or π^*) and a circle of radius 2β, where β is the homoconjugative interaction parameter. In this scheme, the Hückel delocalization energy is zero, regardless of the number of interacting orbitals, thus these systems are *not* homoaromatic. This occurs because the occupied MO's consist of a full set of bonding and antibonding orbitals, with respect to homoconjugative interaction. Without overlap, no net energetic change is predicted. With inclusion of overlap, the overall result should be somewhat destabilizing.

As a test for this simple model, we initially performed extended Hückel molecular orbital (EHMO) calculations[14]

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Table I. Energies for Columnar Structures

structure	E_{total}[a] STO-2G//STO-2G	3-21G//STO-2G	3-21G per $(CH)_4$	MM2 strain per $(CH)_4$[b]
1 ($C_{12}H_{12}$)	-442.31335	-458.60633	-152.86878	34
2 ($C_{16}H_{16}$)	-589.95056	-611.61977	-152.90494	19
3 ($C_{20}H_{20}$)	-737.53746	-764.59463	-152.91893	14

[a] Energies in hartrees. [b] Energies in kcal/mol from ref 6.

on compounds 1–3, using geometries estimated from molecular models and assuming nearly "flat" π bonds. This method was chosen because it includes overlap and has been shown to reliably model homoconjugative interactions. The resultant qualitative pattern of energies which was predicted by these EHMO calculations corresponded quite well to those shown in Figure 2. In each case, net bond orders for homoconjugative interaction were predicted to be nearly zero, consistent with a Hückel level prediction for zero delocalization energy.

Although these extended Hückel calculations clearly demonstrated the effects of columnar homoconjugative interaction, it seemed desirable to proceed to higher level calculations in order to predict geometries. We were particularly interested in the degree of pyramidalization at the double bonds, since this might best predict the isolability of 1–3. Minimal basis set (MBS) ab initio theory was chosen since this generally provides good geometries and should account for effects of through-space interactions. After this work was completed, Sessions and Alder reported MM2 geometries for 1–3.[6]

Computational Methods

Geometries for 1–3 were optimized at the gradient SCF level, with a minimal (STO-2G) basis set and within restriction to D_{3h}, D_{4h}, or D_{5h} symmetry. The program GAMESS was used for all calculations.[15] A gradient tolerance of 0.002 hartree/Bohr was employed. The STO-2G basis generally yields geometries comparable to STO-3G and, in the present case, significantly decreases computer time requirements.

MBS calculations give good geometries but do not yield accurate ionization potentials. For compounds 1–3, a final calculation with the split valence 3-21G basis[16] was performed with the optimized geometries. The 3-21G basis yields a first ionization potential for ethylene of 10.18 eV, which compares favorably with the experimental value (10.51 eV).

Structures 1–3 are $C_{12}H_{12}$, $C_{16}H_{16}$, and $C_{20}H_{20}$, respectively. By previous standards, these are extraordinarily large structures for ab initio studies, and one motivation here was to probe the limits of molecular size which can be treated at this level. In the present cases, there are only two unique carbons (sp^2 and sp^3) and two unique hydrogens [axial (H_a) and equatorial (H_e)] in each structure, due to the high molecular symmetry. This symmetry enormously diminishes the number of integrals, leads to more rapid SCF convergence, and simplifies geometry optimization $2n$-fold. However, even with these simplifications, a 3-21G SCF calculation on 3 (220 basis functions; 140 electrons) generates 7.8 million two-electron integrals. It is obvious that symmetry is a requisite for calculations on such large molecules.

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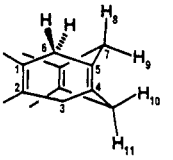
(15) Dupuis, M.; Spangler, D.; Wendoloski, J. J. *NRCC Software Catalog 1*; GAMESS, 1980; Vol. 1, Program QG01.
(16) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

Table II. Optimized Geometric Parameters[a]



parameter	1 (D_{3h})	2 (D_{4h})	3 (D_{5h})
double bond length, Å	1.344	1.337	1.334
allylic bond (C_1–C_6) length, Å	1.562	1.552	1.548
C_1–center (radial) length, Å	1.356	1.724	2.098
π bond separation (C_1–C_5), Å	2.349	2.437	2.465
pyramidalization, Å	43.7	29.3	18.2
angle C_6–C_5–C_7, deg	110.5	119.5	121.8
angle C_2–C_1–C_6, deg	114.3	116.1	117.5
angle H_8–C_7–H_9, deg	107.7	106.9	107.3
flagpole distance H_9–H_{10}, Å	2.631	2.328	2.566

[a] Local numbering scheme is given in structure.

Table III. Cartesian Coordinates for Symmetry Atoms (Bohrs)[a]

	atom	coordinates x	y	z
1 (D_{3h})	C (sp^3)	2.799385	0.0	2.485700
	C (sp_2)	-2.562856	0.0	1.270009
	H_a	2.703176	0.0	4.553471
	H_e	4.792586	0.0	1.950599
2 (D_{4h})	C (sp^3)	2.532125	2.532135	2.551636
	C (sp^2)	3.256629	0.0	1.263231
	H_a	2.352433	2.352433	4.600346
	H_e	3.974500	3.974500	2.199582
3 (D_{5h})	C (sp^3)	4.348488	0.0	2.610534
	C (sp^2)	-3.962974	0.0	1.260373
	H_a	3.914073	0.0	4.635298
	H_e	6.418396	0.0	2.424158

[a] Principal axis is z.

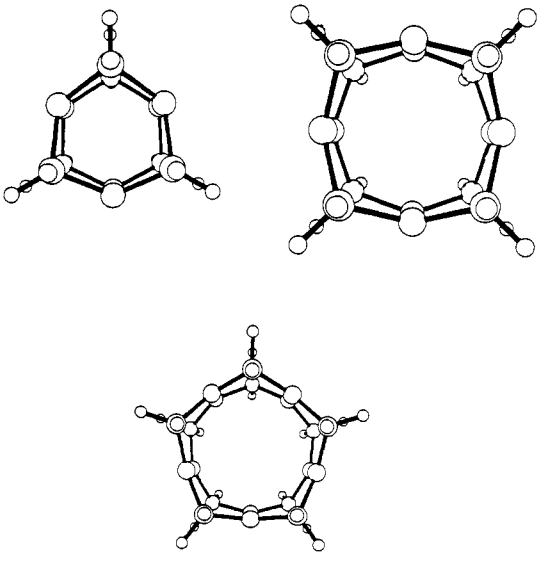


Figure 3. Optimized structures for columnar hydrocarbons 1–3.

Results of Calculations

Total energies and salient geometric parameters for 1–3 are summarized in Tables I and II. Cartesian coordinates for symmetry atoms are collected in Table III. Figure 3 shows top views of the optimized structures. Table I also lists the total energy and strain energy per H_2C—C=C—CH_2 fragment.

Optimized geometries clearly show the expected increase in central cavity size for the series 1–3. This is best measured by the radial distance between the molecular

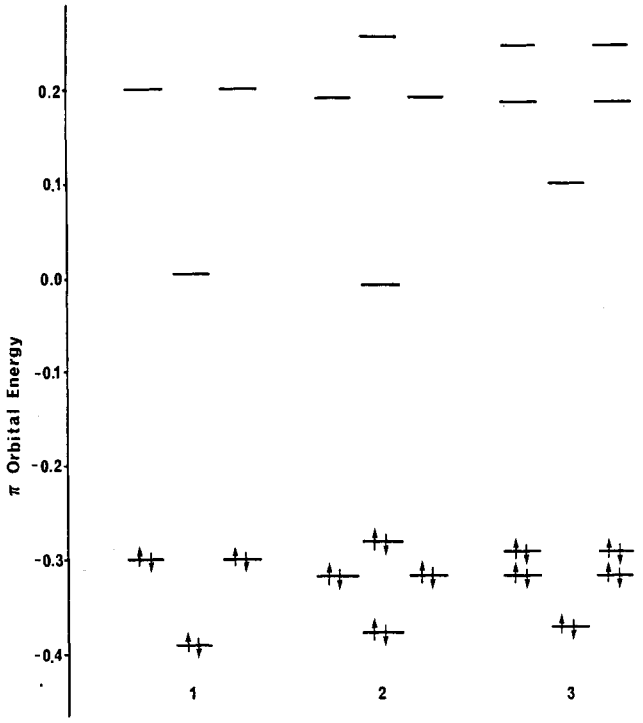


Figure 4. π molecular orbital energies (3-21G SCF) for 1-3.

center (z axis) and sp^2 carbons; predicted values range from 1.36 to 2.10 Å. Despite this increase, the 1,3-π bond separation, i.e., the distance between neighboring sp^2 centers, remains surprisingly constant (2.35–2.47 Å). This constancy is due to counterbalancing effects of pyramidalization (vide infra) at sp^2 centers and increasing ring size.

The pyramidalization at π bonds in structures 1–3 is quite striking; predicted angles are 43.7°, 29.3°, and 18.2°, respectively. These values for pyramidalization are defined as the angle between the vector of the bonded carbons (e.g., C_4–C_5 in Table II) and the C_6–C_5–C_7 plane. In an unpyramidalized π bond, this would be 0°. Sessions and Alder report MM2 pyramidalization angles of 51.6°, 30.3°, and 17.4° for 1–3, respectively, which compare favorably with our values.

There are two potential sources of this π bond pyramidalization. The first is primarily geometric, i.e., torsion imposed by the polycyclic framework. This should be well treated by force field methods. The second is electronic; this arises from closed-shell repulsions due to columnar homoconjugation. The quantitative agreement between ab initio and MM2[6] results implies that π–π interactions have minimal effects on the molecular geometries.

3-21G SCF energies for low-lying molecular orbitals in 1–3 are summarized in Figure 4. Assuming the validity of Koopmans' theorem and neglecting Jahn–Teller effects in ionization from degenerate MO's, the predicted values for ionization potentials which are derived from these orbital energies may be reasonably accurate. In each case, the ordering of molecular orbitals concurs with predictions (Figure 2) from simple perturbation arguments. Both bonding and antibonding levels are ordered in arrays which correspond to those of Hückel monocycles.

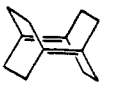
The half-thickness of a π cloud is generally considered to be ca. 1.7 Å; this would be somewhat diminished by pyramidalization outward from the molecular center in 1–3. Both the radial distance (1.356 Å) and π bond separation (2.349 Å) in 1 imply strong through-space interactions. In consideration of these various factors, the interactions in structure 1 are smaller than one might expect. Additionally, the predicted 3-21G ionization potential (8.15 eV) seems unremarkable for a molecule with such strong through-space interaction and distorted q bonds. We attribute both effects to very strong pyramidalization of the π bonds. Orbital distortion will minimize interactions of the endo π bond lobes. Pyramidalization also will mix significant s orbital character into the π bonds, thus lowering the ionization potential. Similar effects have been invoked by Heilbronner to explain the relative insensitivity of alkene and alkyne ionization potentials to twisting and bending.[17] Structures 2 and 4 complete this series in regular fashion.

Conclusions

The effects of homoconjugation should be quite significant in structures 1–3. Through-space π–π interactions lead to strong splitting of π levels, with the resulting pattern essentially as predicted at the one-electron level. These effects are moderated by pyramidalization at the π bonds. Comparison with MM2 results[6] indicates that these interactions do not strongly affect the geometry; pyramidalization is primarily a torsional effect.

Will these molecules prove isolable? As a result of its high degree of π bond pyramidalization (43.7°), we believe that tricolumnar structure 1 will be far too reactive for isolation. However its hexahydro derivative, "iceane" (4), has been known for some years.[10] Dihydro and tetrahydro derivatives bear further exploration.

Pyramidalization in tetracolumnar structure 2 (29.3°) is comparable to that in diene 7 (27.3°). This has been reported by Wiberg[7] as a stable crystalline substance. On



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this basis, one might expect 4 to be isolable. Pentacolumnene (3) is the lowest homologue in the series for which a (slightly strained) Dreiding model may be constructed. The double bonds are predicted by our calculations to be only slightly pyramidalized (18.2°) and the predicted ionization potential and LUMO energy (Figure 4) are unremarkable. Higher homologues should pose no problems.

We are working toward the synthesis of columnar molecules.

Note added in proof: Stoddart and co-workers recently reported the synthesis of structures similar to those described here.[18]

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Ames Laboratory, USDOE, for support of this research. We thank Dr. Stephen Elbert for technical suggestions regarding very large SCF calculations and for running a final calculation on 2.

Registry No. 1, 102097-00-7; 2, 102097-01-8; 3, 102097-02-9.

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