J. Am. Chem. Soc. **1983,** *105,* 2729–2734

Table VII. Carbon NMR Chemical Shifts[a] for Three Pt Complex Ions

C_2[b]	C_6	C_4	C_5	C_3	en
$[Pt(bpy)(en)]^{2+}$ (in D_2O Solution)[c]					
156.93	151.62	142.97	129.52	125.19	48.33
trans-$[Pt(bpy)(en)Cl_2]^{2+}$ (in D_2O Solution)					
155.05	151.30	145.79	131.78	128.09	49.08
$[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]$ (in DMF Solution)					
154.12	150.35	143.35	128.24	125.62	54.62
153.62	149.85	143.02	127.45	124.98	49.89

[a] Chemical shifts in ppm vs. external Me_4Si; measured vs. external Me_4Si or vs. internal DMF. [b] Bipyridyl carbons are conventionally numbered. [c] From ref 24.

II). This means there is even more double bond character in the N–N bonds in the complex nitrosamine than in ordinary nitrosamines and consequently a larger barrier to rotation. By use of the equations developed by Gouesnard and Martin,[23] $\Delta G^{\ddagger}$ for rotation about a 1.283-Å N–N bond can be estimated at 143 kJ/mol, which would mean the effective elimination of such rotations in this complex.

In the crystal one of the bent NNO groups is syn to the five-membered ring's carbons, and the other is anti (Figure 1). From this fact and the large barrier to N–N rotation, it follows, on steric grounds, that the five-membered chelate ring cannot in solution undergo rapid conformational inversion. The process would require the anti NNO to rotate out of the way as it passed the plane of the bipyridyl. The ^{13}C NMR spectrum of $[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]$ is not inconsistent with this conclusion. Every carbon atom in the molecule has a different chemical shift. Table VII shows the ^{13}C δ values in comparison to those of the molecule's two unnitrosated precursors. The bipyridyl ligand resonance assignments follow those of Erickson, Sarneski, and Reilley.[24]

It has been found[20,25] that a given α-carbon resonates at higher field when syn to a nitrosamino than when anti to the same group. The syn–anti differences are in the range of 5–7 ppm. In $[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]$ one of the two en carbon atoms is substantially deshielded upon N,N′-dinitrosation and the other resonates at nearly the same field as before N-nitrosation (Table VII). The deshielded resonance therefore probably comes from the methylene carbon anti to its neighboring nitroso O, that is, C(1).

Acknowledgment. This work was performed on sabbatical leave at the University of New Mexico Department of Chemistry. The assistance of Robert Tapscott and Eileen Duesler is gratefully acknowledged.

Registry No. $[Pt(bpy)(ONNCH_2CH_2NNO)ClNO_2]\cdot 0.5H_2O$, 85116-30-9; $[Pt(bpy)(en)Cl_2]Cl_2$, 85116-31-0.

Supplementary Material Available: A listing of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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Trefoil Aromatics: A Potentially New Class of Aromatic Molecules

T. Fukunaga,* H. E. Simmons, J. J. Wendoloski, and M. D. Gordon

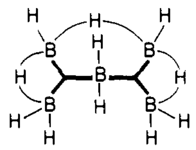
Contribution No. 3091 from the Central Research & Development Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware 19898.

Received July 21, 1982

Abstract: A potentially new class of aromatic molecules termed *trefoil aromatics* is postulated. The system possesses a three-center, two-electron bond (trefoil bond) that is imbedded in the center of an annulene perimeter containing $4n + 2$ π electrons. In a sense, the trefoil bond takes the place of an atom. The concept is generalized to include variations of annulene perimeters and heteroatom incorporation. Also considered are the trefoil cations that result from the center protonation of the trefoil bond. The postulated stability of prototype species is evaluated relative to their valence isomers by molecular orbital calculations.

It is well-known that physicochemical properties of annulenes can be modified significantly by intramolecular union(s) and by enclosing another π system inside the perimeter.[1-3] Recently, annulene perimeters have been considered as a potential host to stabilize novel substructures such as a planar tetracoordinate carbon atom.[4] In this paper we wish to examine a potentially new class of aromatic molecules, *trefoil aromatics*, that incorporates a three-center, two-electron bond within an annulene perimeter containing $4n + 2$ π-electrons.

The three-center, two-electron bonding of interest is now well established and occurs in pentaborane (B_5H_{11}) and higher homologues.[5] One representation of the B_5H_{11} molecule considers the apical BH_2 group to be bound to the remaining four borons in pairs through three-center bonds of the type shown schematically in heavy lines (I). Although there is no really adequate valence-bond description of pentaborane, a molecular orbital



I

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(2) Hellwinkel, D. *Chem.-Ztg.* **1970,** *94,* 715.

(3) The perimeter model[1] to analyze the orbital interactions between an annulene perimeter and an enclosed π system is useful in predicting the stability of condensed cyclic π-electron systems (Fukunaga, T. Third International Symposium on Novel Aromatic Compounds, San Francisco, Aug 1977).

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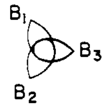
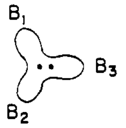
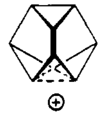
description in terms of the overlap of three hybrid atomic orbitals, one on each boron and directed roughly toward the center of the triangle defined by the borons, accounts nicely for the bonding.



The three resulting MO's are of D_{3h} symmetry, the lowest energy of which is strongly bonding, whereas the remaining two form a degenerate antibonding pair. The stable bonding MO is of trefoil shape and can accommodate two electrons.



This kind of bonding occurs rarely in carbon compounds. The Walsh description of cyclopropane[6] involves three triagonally hybridized carbon atoms overlapping in the central region of the molecule as in B_5H_{11}. This description is, however, basis set dependent and yields the total electron density distribution essentially equivalent to those derived from the alternative models, i.e., the Coulson–Moffitt "bent bond"[7,8] and the Jorgensen–Salem "bond orbital" models,[9] which do not have the trefoil bonding. In fact, X-ray diffraction studies of cyclopropane derivatives[10] and theoretical studies of cyclopropane[11,12] show that the electron density maxima in the ring plane lie outside the triangle and that there is a shallow hole in the center of the ring. There is, however, no compelling reason that the "trefoil bonding" may not be important in certain kinds of organic molecules. For example, multicenter bonding has been suggested to account for the stability and properties of Coates' cation,[13] a rigid, pentacyclic, nonclassical carbonium ion.



Trefoil Aromatics

Carbon normally does not form multicenter bonds of the boron hydride type, in part because of its higher nuclear charge and consequently more contracted AO's. Bonds B–B and B–H are considerably longer than covalent carbon bonds, whose short equilibrium lengths and high binding energies are sufficient to produce very stable structures without recourse to the resonance energy needed to stabilize covalent boron bonds. Three carbon atoms arranged suitably would be expected to form a trefoil bond provided there is some constraining force to prevent reorganization of the bonding to more conventional types. Such a constraining force might be π-electron aromaticity, which could provide the resonance stabilization needed to save the structure from "thermodynamic collapse".

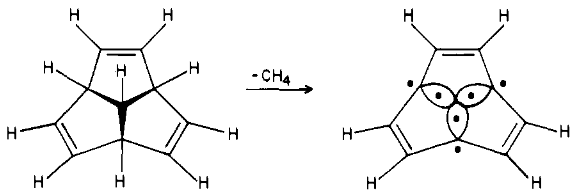
Consider the structure C_9H_6, conceptually formed from cup-shaped triquinacene (**1**)[14] by removing its central CH fragment and the three ring hydrogens at the positions of CH attachment. The resulting molecule has three bare carbon atoms, each with inward-directed trigonal AO's and a p AO. Bond-length considerations indicate that these carbons are abnormally close in the structure **2**, obtained by flattening the ring of nine trigonal carbon atoms. The inward-directed AO's are correctly oriented to form trefoil σ MO's of the following normalized form,

$$\sigma_1 = (1/3^{1/2})(h_1 + h_2 + h_3)$$

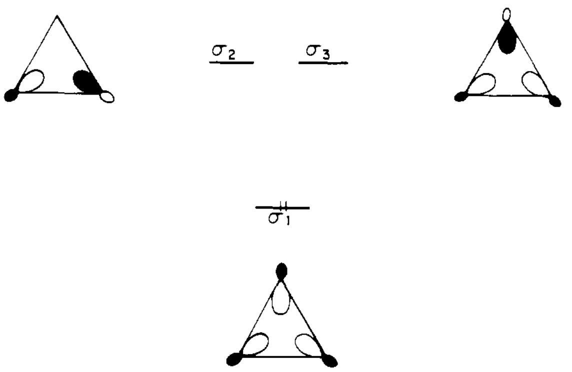
$$\sigma_2 = (1/2^{1/2})(h_1 + h_3)$$

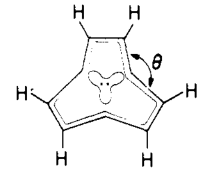
$$\sigma_3 = (1/6^{1/2})(h_1 - 2h_2 + h_3)$$

where h_1, h_2, and h_3 are the trigonal hybrids. σ_1 is a strongly bonding MO, whereas σ_2 and σ_3 are a degenerate antibonding pair; the relative energies are shown in the level diagram. The stable σ_1 MO can accept two of the three electrons formally occupying the hybrids in **2**. The remaining electron must go into an unstable antibonding orbital (σ_2, σ_3), or, most importantly, *it can be promoted to the π system of the ring.* Since the latter contains nine electrons, this promotion is expected to be especially favorable, because a 10π-electron aromatic structure results. We may picture the trefoil aromatic by structure **3**.



1 **2**

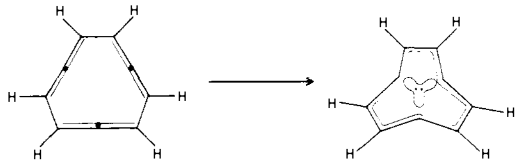




3

$\pi^{10}\ \sigma^2$

[5.5.5]Trefoilene (**3**) is a valence tautomer of the unknown cyclic tris(allene) **4**. Molecular models show that **4** is nonplanar and considerably strained, and bond energy calculations suggest that such electron reorganization would be favorable provided that the trefoil bond contributes 95 kcal/mol. This value would be substantially lowered if the resonance energy of a typical 10π-electron aromatic[15,16] (naphthalene 30.5, $C_9H_9^-$ 14.4 kcal/mol) and the unknown strain energy are included. Thus, should the trefoil bonding be nearly as strong as a covalent C–C bond (which does not seem unreasonable), it would provide a new way to



4 **3**

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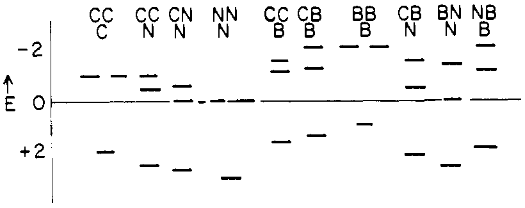
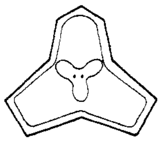
Chart I



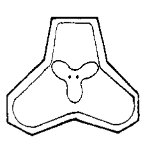
stabilize conventional bonding situations such as aromaticity. In a sense, the trefoil bond *takes the place of an atom.*

Other trefoil hydrocarbons can be envisaged, such as the [5.5.6]-, [5.6.6]-, and [6.6.6]trefoilenes (**5**, **6**, and **7**, respectively).



5

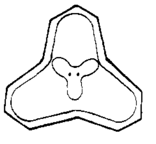
[+] $\pi^{10}\sigma^2$



6

[++] $\pi^{10}\sigma^2$

[− −] $\pi^{14}\sigma^2$



7

[−] $\pi^{14}\sigma^2$

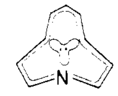
Analysis shows that **5** should exist as the 10π cation and **7** as the 14π anion, with **6** remaining equivocal either the 10π dication or the 14π dianion.

Heterotrefoilenes

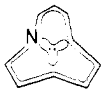
It is easy to construct heterotrefoil aromatics from the consideration already discussed, taking into account the proper valence states of the heteroatoms. The presence of one heteroatom in the trefoil region removes the degeneracy of the σ MO's. For elements more electronegative than carbon, this has the important effect of stabilizing σ_1 and one of the degenerate components (σ_2, σ_3). This further opens the opportunity to reach σ^4 bonding as well as σ^2. Elements electropositive with respect to carbon have the opposite relative effect. Simple MO calculations for boron, carbon, and nitrogen as trefoil atoms give the results shown in Chart I.

Several potential trefoil aromatics are listed in Table I. In all cases, only σ^2 configurations are considered. Thus, an electron in the trefoil region is promoted to the perimeter π system, and the total number of π electrons is, if necessary, adjusted to $4n + 2$ by either adding or removing electron(s). In Table I, the total and perimeter charges are indicated in brackets and parentheses, respectively. For example, the neutral molecules C_9H_6, C_7H_6BN, $C_7H_7N_3$, C_9H_7B, $C_7H_7B_2N$, $C_9H_8N_2$, $C_9H_8B_2$, $C_{11}H_9N$, $C_9H_9B_3$, and $C_9H_9BN_2$ bear a formal positive charge in the σ^2 trefoil region and a negative charge in the perimeter. In others the perimeter may carry a formal zero, positive, or negative charge.

The formal perimeter charge is a useful index of reactivity expected for the species. Generally, low total and perimeter charges might be considered favorable except in the case of the boron derivatives. In the collection in Table I, isomeric structures such as **8** and **9** are not differentiated because their bondings are essentially identical for our present purpose.



8



9

Among the heterotrefoilenes, the boron derivatives are of special interest because of the propensity of boron to form electron-deficient, multicentered bonds. The NBC derivatives are particularly interesting since they are isoelectronic with the parent CCC trefoilenes.

Protonated Trefoilenes

Finally it should be mentioned that the essential feature of trefoil bonding can in principle be maintained if another totally symmetric empty orbital such as the proton s orbital is placed in the center of the trefoil region. The center protonation could provide additional stabilization, particularly to the larger and negatively charged trefoilenes (Chart II).

Table I. Trefoil Aromatics: Total Charge (Brackets), π-Electron Configuration, and Peripheral Charge (Parentheses)

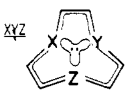
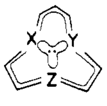
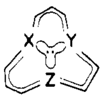
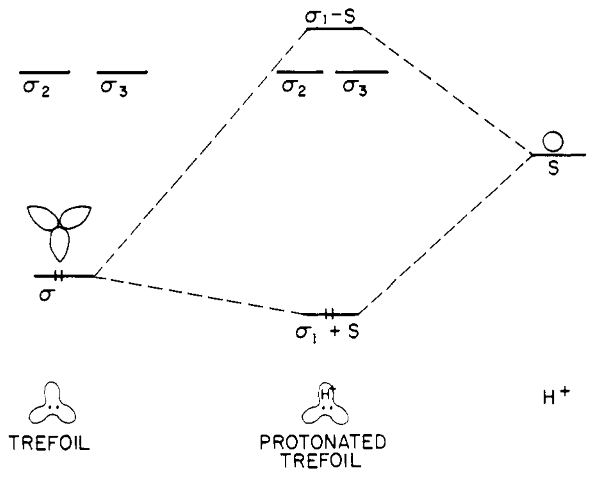
XYZ				
CCC	[0] $\pi^{10}(-1)$	[+] $\pi^{10}(0)$	[++] $\pi^{10}(+1)$ [− −] $\pi^{14}(-3)$	[−] $\pi^{14}(-2)$
CCN	[+] $\pi^{10}(0)$	[++] $\pi^{10}(+1)$	[−] $\pi^{14}(-2)$	[0] $\pi^{14}(-1)$
CNN	[++] $\pi^{10}(+1)$	[−] $\pi^{14}(-2)$	[0] $\pi^{14}(-1)$	[+] $\pi^{14}(0)$
NNN	[−] $\pi^{14}(-2)$	[0] $\pi^{14}(-1)$	[+] $\pi^{14}(0)$	[++] $\pi^{14}(+1)$
CCB	[−] $\pi^{10}(-2)$	[0] $\pi^{10}(-1)$	[+] $\pi^{10}(0)$	[− −] $\pi^{14}(-1)$
CBB	[++] $\pi^{6}(+1)$ [− −] $\pi^{10}(-3)$	[−] $\pi^{10}(-2)$	[0] $\pi^{10}(-1)$	[+] $\pi^{10}(0)$
BBB	[+] $\pi^{6}(0)$	[− −] $\pi^{10}(-3)$	[−] $\pi^{10}(-2)$	[0] $\pi^{10}(-1)$
CBN	[0] $\pi^{10}(-1)$	[+] $\pi^{10}(0)$	[− −] $\pi^{14}(-3)$	[−] $\pi^{14}(-2)$
BBN	[−] $\pi^{10}(-2)$	[0] $\pi^{10}(-1)$	[+] $\pi^{10}(0)$	[− −] $\pi^{14}(-3)$
BNN	[+] $\pi^{10}(0)$	[++] $\pi^{10}(+1)$ [− −] $\pi^{14}(-3)$	[−] $\pi^{14}(-2)$	[0] $\pi^{14}(-1)$

Chart II



Molecular Orbital Calculations

The postulated stability of trefoil bonding was initially probed by MINDO/3[17] calculations of [5.5.5]trefoilene (**3**) and its centrally protonated cation, $C_9H_7^+$, and was further investigated by ab initio treatment using the program GAMESS.[18]

A. C_9H_6. In MINDO/3 scouting calculations, atoms were held in a plane with D_{3h} symmetry and standard bond lengths were assumed, $d_{C-C} = 1.40$ Å and $d_{C-H} = 1.10$ Å. The bond angle (θ) of the trefoil carbon atoms was then decreased from linearity in 10° increments. The results are shown in Figure 1, and salient features may be summarized: (1) The trefoil bent structure is at energy minimum within the framework of D_{3h} structure. The minimum energy form is predicted to be a bent ~150° configuration that is 22 kcal/mol more stable than the 180° structure **4**. A substantial stabilization of the trefoil σ orbital (>3 eV) contributes in large part to the overall stability. (2) Irrespective of the angle θ, the π framework bears 10π electrons carrying a unit negative charge, which is compensated by a unit positive charge in the σ framework. The trefoil carbon atoms, however, become more electron deficient as the angle θ becomes more acute

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[17] Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302, 1307. Dewar, M. J. S.; Lo, D. H.; Ramsden, C. A. *Ibid.* **1975**, *97*, 1311.

[18] Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC Program QG01.

Table II. Ab Initio Energies of C_9H_6 **3**[a]

	level					
	4-31G	STO-3G		4-31G[d]		6-31G*
symmetry	D_{3h}	D_{3h}	C_{3v}	D_{3h}	C_{3v}	C_{3v}
θ	180.00°	148.35°	148.33°	156.56°	156.56°	156.56°
Total Energy, au						
	−343.388016	−339.683228	−339.68347	−343.463044	−343.463044	−343.960636
Heat of Formation,[b] kcal/mol						
ΔH_f^A	327			280	280	289
ΔH_f^B	297			250	250	278
MO Energies,[c] eV						
LUMO + 1	3.02 (π)	6.68 (σ)†		3.21 (π)		3.21 (π)
LUMO	1.43 (σ)†	5.94 (π)		3.12 (σ)†		3.17 (σ)†
HOMO	−5.44 (σ)	−4.64 (π)†		−6.68 (π)†		−6.63 (π)†
HOMO − 1	−7.15 (π)†	−9.19 (σ)		−9.37 (σ)		−9.37 (σ)

[a] Calculated by using the geometries described in the supplementary material. The 4-31G optimized geometry was used for 6-31G* calculation. [b] See eq 1 and 2 in the text. [c] † Indicates double degeneracy. [d] Gross charges on H, trefoil, and trigonal carbons are +0.13, +0.06 (σ +0.21, π −0.15), and −0.16 (σ −0.09, π −0.07), respectively.

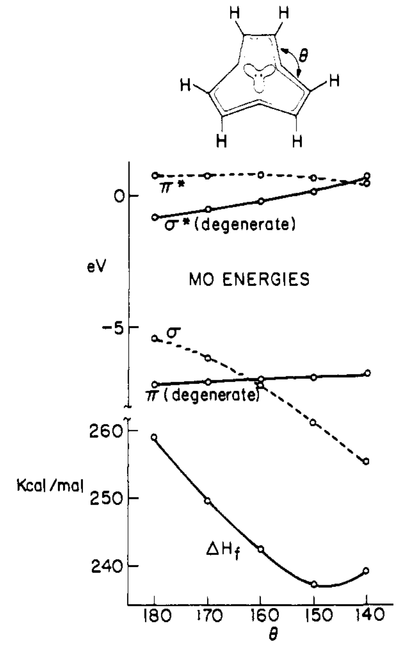
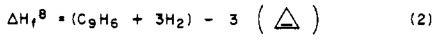


Figure 1. Heat of formation and frontier orbital energies of [5.5.5]trefoilene calculated by MINDO/3.

mainly because of σ-electron reorganization. (3) The π bond order increases between the trefoil and the trigonal carbon atoms but decreases between the two trigonal carbon atoms as θ decreases.

In order to further evaluate the details, complete geometric optimizations were carried out at the STO-3G[19a] and 4-31G levels.[19b] At both levels, the energy minimum form is calculated to be slightly nonplanar, and the bent angle θ is predicted to be 148.3° and 156.6° at the STO-3G and 4-31G level, respectively. Orbital ordering calculated at the 4-31G level is similar to that of MINDO/3, whereas they differ significantly from the STO-3G results (Table II). Calculations at the 6-31G level using the 4-31G optimized structure essentially reproduce the 4-31G results. The heat of formation of the C_9H_6 trefoilene was evaluated by the thermochemical equations (1) and (2) using heats of formation



calculated for reference compounds with the respective basis sets.

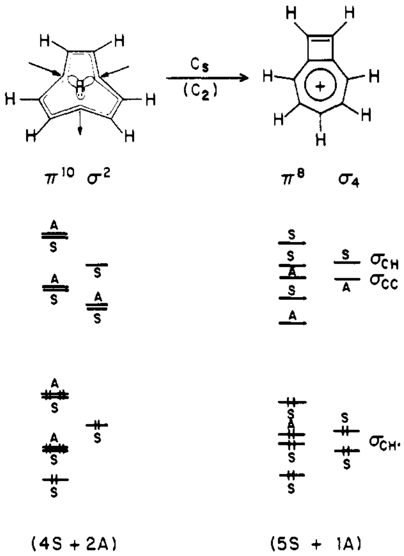


Figure 2. An orbital correlation diagram (MINDO/3) for valence isomerization, **11** ⇄ **12**, under C_s operation.

As summarized in Table II, the two ΔH_f values converge as the size of basis sets increases. The ΔH_f^A value with 6-31G* basis sets, 289 kcal/mol, is the most reliable one, and ΔH_f^A (4-31G) values may be good enough for comparison purposes. At the latter level the 156.6° bent form is 47 kcal/mol more stable than the 180° structure. Undoubtedly, a substantial part of the stabilization results from the significant energy lowering of the trefoil σ orbital, amounting to almost 4 eV. Charge separation between the σ and π systems (0.87) is not as large as the corresponding MINDO/3 value (1.00). However, the trefoil carbon atoms are electron deficient, particularly in the σ framework, in accord with the MINDO/3 prediction.

It is interesting to note that whereas the highest occupied molecular orbital (HOMO) is clearly a doubly degenerate π orbital, the low-lying unoccupied orbitals consist of a doubly degenerate trefoil σ^*-orbital pair (ϵ 3.17 eV) and a π^* orbital (ϵ 3.21 eV). Thus, the molecule may display absorptions due both to $\pi^* \leftarrow \pi$ and to $\sigma^* \leftarrow \pi$ transitions.

Although the calculations discussed above predict that the trefoil structure is stable to deformations that maintain the C_3 symmetry axis, its relationship with respect to the entire energy surface is not known. In search of more stable valence isomers, we have found that the unknown bicyclic carbene **10** is 74 kcal/mol (4-31G) more stable than the C_{3v} trefoilene structure. Thus, the latter could be isolable only if it is protected by sufficient energy barriers

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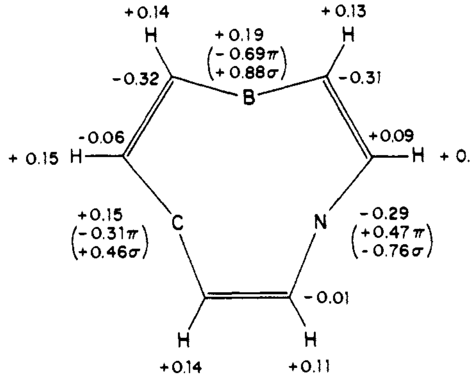
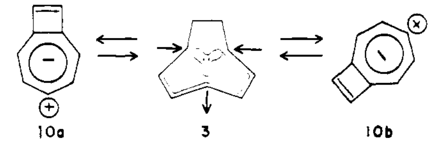
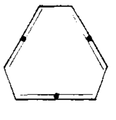


Figure 3. 4-31G gross charges of C_9H_6BN.

from going to **10**; otherwise it may represent the transition state for the degenerate rearrangement (**10a** ⇄ **10b**). The valence tautomerization, **3** ⇄ **10**, could take place through deformation involving only the σ framework, in which one of the trefoil carbon atoms is pushed outward while the other two are pushed in. In this way, the 10π-electron stabilization can be maintained throughout. Furthermore, the trefoil σ orbitals (σ_1, σ_2, and σ_3) are smoothly transformed into the (σ and σ^*) orbitals of the newly formed C–C bond and an unoccupied σ orbital at the carbene center. The bicyclic carbene **10** is predicted to be nonplanar by MINDO/3, and the energies reported above are calculated for the MINDO/3 optimized geometry.



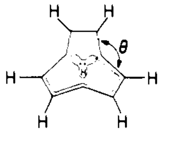


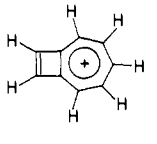
	10a	3	10b	4
ΔH_f (kcal/mole)				
MINDO/3		237	143	259
4-31G		280	206	327

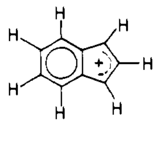
B. $C_9H_7^+$. The structure of the $C_9H_7^+$ cation has been of interest to us since this species is observed as the most abundant fragment ion in the mass spectrum of triquinacene.[14,20] As one of the possible structures, we have investigated the centrally protonated trefoil cation structure **11**.

The STO-3G optimized structure has the 167° bent angle θ that is considerably larger than the corresponding angle in the neutral trefoilene (**3**). It is nonplanar (C_{3v}) and deviates from planarity slightly more than **3**.

MINDO/3 predicts, however, that the trefoil cation **11** is considerably less stable ($\sim$100 kcal/mol) than the isomeric bicyclic cations **12** and **13**. Of the latter, π-electron thermocyclic calculations[21] predict also that **13** is more stable than **12** by 7.5 kcal/mol. Although **11** is predicted to be much less stable than **12**, the tautomerization process deserves further consideration.

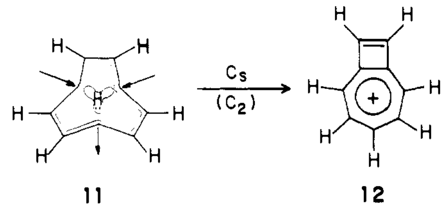




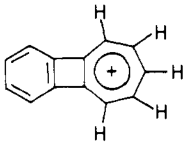


	11	12	13
ΔH_f (kcal/mole) MINDO/3	351 (θ = 170°) 361 (θ = 180°)	257	253

Unlike the valence isomerization, **3** ⇄ **10**, the direct conversion, **11** → **12**, must involve σ–π mixing while the 10π system is transformed into a 8π-electron system with concomitant formation of a C–C and a C–H covalent bond. An orbital correlation diagram depicted in Figure 2 for the relevant orbitals involved in the transformation under C_s symmetry shows that the valence isomerization is thermally forbidden. A similar process under C_2 symmetry is also forbidden. Thus, the cation generated in the trefoil geometry may not readily isomerize to the bicyclic structure **12**, and vice versa. It is interesting to note that a benzoannelated derivative (**14**) of **12** has been isolated[22] as stable purple crystals, but its isomerization to the trefoil cations has never been considered.



11 **12**



14

C. C_7H_6BN. Heterotrefoilene **3** (X, Y, Z = C, N, B) isoelectronic with the homocyclic [5.5.5]trefoilene was briefly examined by 4-31G using the C_9H_6 (D_{3h}) geometry. As expected, the trefoil σ MO's are no longer degenerate and consist of a bonding occupied MO (−10.53 eV) and two highly split antibonding MO's (+1.43, +5.51 eV). The π orbitals are also nondegenerate and include two relatively high-lying occupied (−7.28, −6.24 eV) and low-lying unoccupied MO's (+3.12, +3.64 eV). The molecule is thus expected to be highly electrophilic because of the low-lying trefoil LUMO (+1.43 eV). Another salient feature of this molecule is the sizable electron transfer from the boron and carbon atoms to the trefoil nitrogen atom in the σ framework and π back-donation from the latter to the former (see Figure 3).

Concluding Remarks

The trefoil bonding postulated in this paper is apparently novel, and molecular quantum mechanical calculations show that the [5.5.5]trefoilene (**3**) and its centrally protonated cation (**11**) are slightly nonplanar and stable to C_3-symmetry deformations. Bond alternation in the perimeter is small, suggesting structural aromaticity. Although thermochemically more stable valence tautomers exist for the prototype trefoils that we have investigated, some of these structures should at least be observable as reactive intermediates and may be capable of isolation. While we have not investigated them, other means such as steric constraints and substituents may further stabilize the trefoil systems. The discovery of the trefoil aromatics would be of fundamental interest and broaden the scope of structural organic chemistry.

Registry No. **3**^{0} (XYZ = CCC), 84598-41-4; **3**$^+$ (XYZ = CCN), 85115-88-4; **3**$^{2+}$ (XYZ = CNN), 85115-89-5; **3**$^-$ (XYZ = NNN), 85115-90-8; **3**$^-$ (XYZ = CCB), 85115-91-9; **3**$^{2+}$ (XYZ = CBB), 85115-92-0; **3**$^+$ (XYZ = BBB), 85115-93-1; **3**^{0} (XYZ = CBN), 85115-94-2; **3**$^-$ (XYZ = BBN), 85115-95-3; **3**$^-$ (XYZ = BNN), 85115-96-4; **5**$^+$ (XYZ = CCC), 85115-97-5; **5**$^{2+}$ (XYZ = CCN), 85115-98-6; **5**$^-$ (XYZ = CNN), 85115-99-7; **5**^{0} (XYZ = NNN), 23635-82-7; **5**^{0} (XYZ = CCB), 85116-00-3; **5**$^-$ (XYZ = CBB), 85134-93-6; **5**$^{2-}$ (XYZ = BBB), 85116-01-4; **5**$^+$ (XYZ = CBN), 85116-02-5; **5**^{0} (XYZ = BBN), 85116-03-6; **5**$^{2+}$ (XYZ = BNN), 85116-04-7; **5**$^{2-}$ (XYZ = BNN), 85116-05-8; **6**$^{2+}$ (XYZ = CCC), 85116-06-9; **6**$^{2-}$ (XYZ = CCC), 85116-07-0; **6**$^-$ (XYZ = CCN), 85116-08-1; **6**^{0} (XYZ = CNN), 85116-09-2; **6**$^+$ (XYZ = NNN), 85116-10-5; **6**$^+$ (XYZ = CCB), 85116-11-6; **6**^{0} (XYZ = CBB), 85116-12-7; **6**$^-$ (XYZ = BBB), 85116-13-8; **6**$^{2-}$ (XYZ = CBN), 85116-14-9; **6**$^+$ (XYZ = BBN), 85116-15-0; **6**$^-$ (XYZ = BNN), 85134-94-7; **7**$^-$ (XYZ = CCC), 85116-16-1; **7**^{0} (XYZ = CCN), 85116-17-2; **7**$^+$ (XYZ = CNN), 85116-18-3; **7**$^{2+}$ (XYZ

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= NNN), 85116-19-4; 7^{2-} (XYZ = CCB), 85116-20-7; 7^{+} (XYZ = CBB), 85116-21-8; 7^{0} (XYZ = BBB), 85116-22-9; 7^{-} (XYZ = CBN), 85116-23-0; 7^{2-} XYZ = BBN, 85116-24-1; 7^{0} XYZ = BNN, 85116-25-2; **10b**, 85116-26-3; **12**, 85116-27-4; **13**, 85116-28-5; $C_9H_7^+$, 84598-40-3.

Supplementary Material Available: Tables listing MINDO/3 heat of formation, MO energies, charge densities, π-bond order, and ab initio optimized geometric parameters of [5.5.5]trefoilene, MO energies (4-31G, MINDO/3) of the bicyclic carbene **10**, and STO-3G optimized geometries and MO energies of the protonated trefoilene $C_9H_7^+$ (4 pages). Ordering information is given on any current masthead page.

Ester Aminolysis: New Reaction Series for the Quantitative Measurement of Steric Effects

DeLos F. DeTar* and Claire Delahunty

Contribution from the Department of Chemistry, The Florida State University, Tallahassee, Florida 32306. *Received September 16, 1982*

Abstract: Further development of theoretical methods for computing steric effects on chemical reactivity requires a large body of new reliable quantitative data for calibration and for testing. We report here on design criteria for reaction series suitable for obtaining these data and on a successful implementation that shows promise of providing access to a particularly broad range of steric hindrance and which additionally has shown a new form of steric hindrance. The series examined in the present study is ester aminolysis in the form $RCOOC_6H_4NO_2$-*p* + $R'NH_2$ in acetonitrile solution. A primary purpose of the examination has been to ascertain whether aminolysis may be a useful general series or whether known or unexpected complications might render it unsuitable. We have measured rate constants for a matrix of reactions using five different R groups and four different R′ groups, each reaction at a series of concentrations of amine. This is the first systematic study of the simultaneous action of steric hindrance effects in both the acylating agent and the entering nucleophile. The reactions showed both a second-order term k_2[ester][amine] and a relatively less important third-order term k_3[ester][amine]^2. The Taft equation was applied to subsets of the rate constants. For each amine there were data for a set of esters for which the R group was the variable. The slopes ρ_s for these sets were nearly unity. For each ester there were corresponding data for a series of amine reactions in which R′ was the variable. These sets also gave good correlations, but the slopes ρ_s' were considerably larger, about 2.3. This unusually large difference in response to structural effects in the acylating agent and in the nucleophile is unexpected and appears to arise from a new type of steric hindrance. An obvious explanation based on bond lengths proves to be quantitatively insufficient; that explanation postulates that there is greater hindrance for the amine because the C–N bond is short in comparison with the C–C bond. The difference may be due instead to a requirement for special orientation within the transition state, a matter currently under theoretical investigation. The k_2 and the k_3 sets gave similar correlations, an important finding in at least two respects. It means that steric effects are well-defined in this example of ester aminolysis, and it means also that the extra molecule of amine is far enough from the reaction center so that no additional steric hindrance results. The reactions observed in the present study cover a range of 5 powers of 10 in relative rate constants. Preliminary studies with other examples of aminolysis suggest that a range of relative rate constants covering well in excess of 12 powers of 10 should be observable.

Although steric effects can cause enormous variations in reactivity, quantitative studies have never achieved popularity. This neglect may be contrasted with the widespread interest in the investigation of polar effects. A major deterrent to the study of steric effects has been lack of general quantitative treatments. Linear free energy relationships (LFER) among sets of equilibria or of rates have generally been successful for gaining a quantitative correlation of polar effects. Although LFER treatments are also applicable to certain types of steric effects, the range of applicability is limited.

The most successful linear free energy treatments of steric effects are based on the Taft E_s constants or their derivatives.[1-4] A general form of the Taft expression, a linear free energy relationship, is shown in eq 1.[5,6] The σ_I constants are the polar

$$\log k = a + \rho_I\sigma_I + \rho_s E_s \qquad (1)$$

substituent constants applicable to saturated systems; $\sigma_I = \sigma^*/6.22$ while ρ_I and ρ_s are the LFER slopes. Equation 1 was originally derived for ester hydrolysis. It has proved generally applicable to esterification and ester hydrolysis and to a few other classes of reactions as well, certain forms of the Menschutkin reaction being an example.[3,7] Where applicable, the Taft equation provides a good starting point for the analysis of steric effects on reaction rates and equilibria.

Within the past few years our potential ability to predict steric effects has changed dramatically.[8-24] It appears now that it is

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