A Perturbational Molecular Orbital (PMO) Theory of Homoaromaticity

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Abstract: It is shown that much of the chemistry of homoaromatic molecules may be described by the PMO theory. In addition, the theory leads to some interesting predictions regarding hitherto unknown systems.

The PMO method has been developed into a powerful theory of organic chemistry by Dewar[2] from concepts originally introduced by Coulson and Longuet-Higgins.[3] The method has been applied to a wide range of problems with impressive results, particularly in the area of aromatic character in ground state molecules and the transition states of chemical reactions.[2c-e] The reasons for the success of the PMO method and its superiority to the simple Hückel MO (HMO) method on which it is based have been discussed[2] and it will not be necessary to reproduce these arguments here. Rather, we briefly note below some of the features of the analysis which are salient to our treatment of homoaromaticity.

The PMO treatment is concerned with differences in the properties of structurally related molecules, rather than the absolute values of the quantities relating to the individual molecules. Actually, by an appropriate choice of the reference system it will prove possible to obtain the information we require directly, in a very simple and straightforward manner which preserves a close understanding of the chemistry involved. Thus we are not so much concerned with the absolute values of the energy, charge densities, and bond orders of the homotropenylium cation, but rather the way in which these quantities differ from the parent tropenylium cation. In the PMO treatment this information is extracted by considering the homotropenylium cation to be a perturbed form of the tropenylium cation in which the resonance integral of one bond is reduced, as a result of the homoconjugate linkage (Figure 1). From simple concepts such as this it will prove possible to describe much of the chemistry of known homoaromatic molecules[4] and to make some predictions regarding hitherto unknown systems.

The few published theoretical and physicochemical treatments of homoaromaticity[5] have been primarily concerned with information of the first kind (absolute values), and are thus complementary to the present study, although we refer to them where they are appropriate to the discussion.

Theory

In the HMO theory[6,7] E the π electron energy (in the absence of perturbations) is given by

$$E(\alpha_i, \beta_{ij}) = \sum_i^{\text{all atoms}} q_i\alpha_i + 2\sum\sum_{i<j}^{\text{all atoms}} p_{ij}\beta_{ij} \tag{1}$$

where α_i is the coulomb integral of atom i, and β_{ij} is the resonance integral between atoms i and j.

The electron density (q_i) and bond order (p_{ij}) are given by

$$q_i = 2\sum_\mu^{\text{occ}} a_{\mu i}^2 \tag{2}$$

$$p_{ij} = 2\sum_\mu^{\text{occ}} a_{\mu i}a_{\mu j} \tag{3}$$

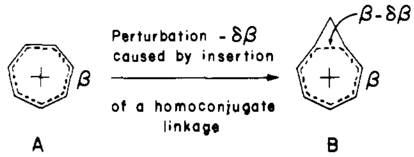

Figure 1. PMO picture of the change in resonance integral due to the perturbation of the parent system A by the insertion of a homoconjugate linkage to give homoaromatic B (exemplified by the tropenylium case).

where $a_{\mu i}$ is the coefficient of the atomic orbital (AO) ϕ_i in the MO ψ_μ.

$$\psi_\mu = \sum_i^{\text{all atoms}} a_{\mu i}\phi_i \tag{4}$$

If the coulomb and resonance integrals are subject to perturbations $\delta\alpha_i$ and $\delta\beta_{ij}$, respectively, then (to second order) the energy may be expanded in a Taylor series about E^0 to give

$$E(\alpha_i + \delta\alpha_i, \beta_{ij} + \delta\beta_{ij}) = E^0 + \sum_i \frac{\partial E}{\partial\alpha_i}\delta\alpha_i + \sum_{ij}\frac{\partial E}{\partial\beta_{ij}}\delta\beta_{ij} + {}^1\!/_2\sum_i\sum_j\frac{\partial^2 E}{\partial\alpha_i\partial\alpha_j}\delta\alpha_i\delta\alpha_j + {}^1\!/_2\sum_{ij}\sum_{kl}\frac{\partial^2 E}{\partial\beta_{ij}\partial\beta_{kl}}\delta\beta_{ij}\delta\beta_{kl} + \sum_{ij}\sum_k\frac{\partial^2 E}{\partial\beta_{ij}\partial\alpha_k}\delta\beta_{ij}\delta\alpha_k \tag{5}$$

the summations being over perturbed atoms and bonds.

The first derivatives follow from the differentiation of eq 1

$$\partial E/\partial\alpha_i = q_i$$

$$\partial E/\partial\beta_{ij} = 2p_{ij}$$

whereas the second derivatives are the atom-atom, bond-bond, and bond-atom polarizabilities, symbolized by $\Pi_{i,j}$, $\Pi_{ij,kl}$, and $\Pi_{ij,k}$, respectively, and are obtained from the perturbed wave function.[6] Thus eq 5 becomes

$$E = E^0 + E^1 + E^2 \tag{6}$$

where E^0 is given by eq 1, and

$$E^1 = \sum_i q_i\delta\alpha_i + 2\sum_{ij}p_{ij}\delta\beta_{ij} \tag{7}$$

$$E^2 = {}^1\!/_2\sum_i\sum_j\Pi_{i,j}\delta\alpha_i\delta\alpha_j + \sum_{ij}\sum_{kl}\Pi_{ij,kl}\delta\beta_{ij}\delta\beta_{kl} + 2\sum_{ij}\sum_k\Pi_{ij,k}\delta\beta_{ij}\delta\alpha_k \tag{8}$$

where the superscript denotes the order of the perturbation. Similarly, the perturbed electron densities and bond orders are given by

$$q_k = q_k^0 + q_k^1 \tag{9}$$

where

$$q_k^1 = \sum_i \Pi_{i,k}\delta\alpha_i + 2\sum_{ij}\Pi_{ij,k}\delta\beta_{ij} \tag{10}$$

and

$$p_{ij} = p_{ij}^0 + p_{ij}^1 \tag{11}$$

where

$$p_{ij}^1 = \sum_k \Pi_{ij,k}\delta\alpha_k + \sum_{kl}\Pi_{ij,kl}\delta\beta_{kl} \tag{12}$$

The perturbations $\delta\alpha_i$ and $\delta\beta_{ij}$ are introduced into these equations as fractions of the resonance integrals β_{ij}, which, without loss of generality, may usually be assumed to have a common value β (negative quantity). It will rarely be necessary to ascribe a magnitude to $\delta\alpha_i$ or $\delta\beta_{ij}$ merely to the sign of the perturbation (for a homoconjugate linkage, of course $-\delta\beta$ will be appropriate), and we shall usually be able to drop the subscripts without ambiguity. Within these definitions a positive energy change is stabilizing and a negative energy change destabilizing.

The polarizabilities are obtained in units of $(\beta)^{-1}$, and thus all energies will be implicitly expressed in units of β. For convenience it will be easier to work with charge densities (ζ_k), rather than electron densities.[8] For a π-electron monovalent atom such as carbon

$$\zeta_k = 1 - q_k \tag{13}$$

and eq 9 and 10 become

$$\zeta_k = \zeta_k^0 + \zeta_k^1 \tag{14}$$

and

$$\zeta_k^1 = -\sum_i \Pi_{i,k}\delta\alpha_i - 2\sum_{ij}\Pi_{ij,k}\delta\beta_{ij} \tag{15}$$

With this definition the charge densities reflect the net charge of the atom (carbonium ions have positive ζ_k, carbanions negative ζ_k).

In the remainder of the paper we show how the factors affecting homoaromatic character may be assessed by use of the above relations.

First Order Effects

The Influence of a Single Homoconjugate Linkage on the π-Electron Energy. The starting point used throughout this work is the parent aromatic molecule, which is assumed to be completely delocalized with a common overlap integral (β) for all pairs of conjugated carbon atoms (Figure 1). Homoconjugate linkages are introduced as a perturbation of the parent by a change $-\delta\beta_{ij}$ in the appropriate resonance integral. Thus to first order, the change in energy (from eq 7) is given by

$$E^1(-\delta\beta) = -2p_{ij}\delta\beta \tag{16a}$$

Although the first-order contribution will be dominant, we shall also include the second-order energy change (from eq 8) which is given by

$$E^2(-\delta\beta, -\delta\beta) = \Pi_{ij,ij}\delta\beta^2 \tag{16b}$$

Some representative values of these energy changes are given in Table I. All of the homoaromatic species which are presently known[4] (with the exception of annelated derivatives, discussed later) are derived from parent systems with high symmetry and a common bond order between all the ring carbon atoms (**1**–**6**) and thus the position of the homoconjugate linkage has no influence on the final energy.

The perturbed energies in Table I can also be interpreted in terms of the resonance energy of the parent aromatic system, for at $\delta\beta = 1$ they correspond to the destabilization on conversion to the open chain analog.[9] In the context of homoaromaticity, however, the value of $\delta\beta$ is assumed to lie in the range $0 < \delta\beta < 1$.

Table I. E^1 and E^2 Values for the Insertion of a Homoconjugate Linkage

Patent system[c]	$E^1(\times 1/\delta\beta)^b(\beta)$	$E^2(\times 1/\delta\beta^2)^c(\beta)$
1	−1.3333	0.1481
2	−1.2944	0.2316
3	−1.2840	0.2693
4	−1.2797	0.2905
$15[A]^+$	−1.2756	0.3200
$17[A]^-$	−1.2751	0.3252
$4[A]^{2+,2-}$	−1.0	0.2500
$\mathbf{5}^{2+,2-}$	−1.2071	0.3049
$12[A]^{2+,2-}$	−1.2440	0.3214
$16[A]^{2+,2-}$	−1.2568	0.3303
6	−1.3333	0.2407
10[A]	−1.2944	0.2922
14[A]	−1.2840	0.3137
18[A]	−1.2797	0.3253

[a] See eq 16a. [b] See eq 16b. [c] A = annulene.

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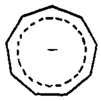

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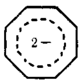

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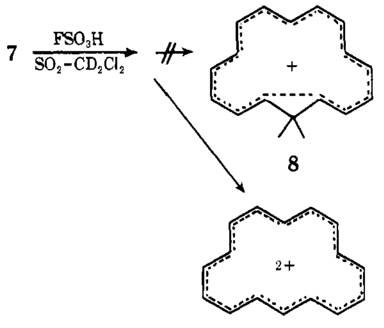
While detailed comparisons between the various systems in Table I are not really justified (due to variations of β with charge[2,10]), some trends are obvious. Most noticeable is the decrease in the drive for conjugation as evidenced by the reduction in magnitude of the sum of the perturbed energies at higher ring sizes, brought about by a decrease in the first-order term (with the exception of the dications and dianions of [4*n*]annulenes), and an increase in the second-order term. This latter, of course, will only be important for large $\delta\beta$, but the trend does indicate that at large ring sizes the gain in resonance energy accompanying homoaromatization[11] may be too small to offset the strain energy inherent in the formation of the homoconjugate bridge. When these factors are considered in conjunction with the expectation that the resonance energies of the planar, unbridged annulenes will fall away to zero at large ring sizes,[15,16] it becomes apparent that the maximum ring size for homoaromatization may be quite low. In fact, the work of Oth, Smith, Prange, and Schröder[17] suggests that this limit may have already been reached, for they showed that the dissolution of [16]annulene (**7**) in FSO_3H which was expected to lead to the homo[15]annulenium cation (**8**) gave rise instead to the [16]annulenium dication (**9**), via an oxidative pathway.



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This observation is even more striking in view of the suggestion[18] that the difficulty experienced in the synthesis of the cyclobutadienium[19] and cyclooctatetraenium[20] dications from appropriately substituted precursors was brought about by the intervention of the homocyclopropenium and homotropenylium cations, respectively.

Second-Order Effects

1. The Influence of a Second Homoconjugate Linkage on Homoaromatic Stability. In the presence of a second homoconjugate linkage (assuming $\delta\beta_{ij} = \delta\beta_{kl} = -\delta\beta$) the perturbed energies (from eqs 7 and 8) are given by:

$$E^1(-\delta\beta, -\delta\beta) = -2p_{ij}\delta\beta - 2p_{kl}\delta\beta \qquad (17)$$

$$E^2(-\delta\beta, -\delta\beta) = \Pi_{ij,ij}\delta\beta^2 + \Pi_{kl,kl}\delta\beta^2 + 2\Pi_{ij,kl}\delta\beta^2 \qquad (18)$$

With molecules of high symmetry (**1**–**6**), these equations may be reduced to:

$$E^1(-\delta\beta, -\delta\beta) = -4p_{ij}\delta\beta \qquad (19)$$

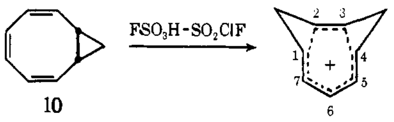
$$E^2(-\delta\beta, -\delta\beta) = 2\Pi_{ij,ij}\delta\beta^2 + 2\Pi_{ij,kl}\delta\beta^2 \qquad (20)$$

As may be seen by comparison with eq 16a and 16b, the effects of two homoconjugate linkages are additive, apart from the cross term in eq 20. It is this latter term with which we shall be concerned in this section, and we symbolize it by:

$$E^2_{ij,kl}(-\delta\beta, -\delta\beta) = 2\Pi_{ij,kl}\delta\beta^2 \qquad (21)$$

This term provides a measure of the energy of interaction of the two homoconjugate linkages, and thus will indicate how these linkages may be best disposed in the ring to bring about the most favorable π-electron energy change (see Table II). It is not suggested that the only bishomoaromatic compounds will be those with a favorable $E^2_{ij,kl}$ value. This is a second-order term, and its effect will in general be small; nevertheless, where a molecule has a choice in the relative disposition of homoconjugate linkages, and where the steric requirements are not unreasonable, we might expect this term to be determining.

Of the bishomoaromatic molecules which are known,[4,5e] most have the homoconjugate linkages in a predetermined sequence owing to the precursors used. Examples are known with both positive[21] and negative[22] values of the coupling term (eq 21). It should be noted that these latter cases will experience greater drive for homoaromatization (minimization of $\delta\beta$), as they suffer a greater destabilization due to the presence of the coupling term. Bearing in mind, however, that $\delta\beta$ cannot be reduced to zero in homoconjugate linkages,[16] where the opportunity exists we would expect the preferential formation of bishomoaromatic systems with positive $E^2_{ij,kl}$ values. Such a case has in fact been observed with the protonation of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**10**) to give the 1,3-bishomotropenylium cation (**11**),[23a] although the question as to whether **11** is formed under kinetic or thermodynamic control does not appear to have been completely resolved.[21b] Nevertheless, the formation of **11** is in agreement with the predictions of eq 21 and with the resonance arguments and HMO calculations given by Ahlberg and coworkers.[5e]



10 **11**

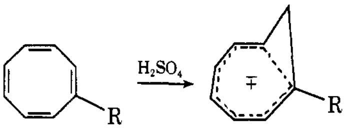
2. The Influence of Substituents on Homoaromatic Stability. In order to assess where substituents are best placed with respect to the homoconjugate linkage, we shall assume that the most important effect is a change ($\delta\alpha_i$) in the coulomb integral (α_i) at the site of substitution in the ring.[24,26]

Again, we shall only be concerned with the interaction term between homoconjugate linkage and substituent, as it is only this contribution which depends on their relative orientation in the ring. From eq 8, this is given by

$$E^2_{ij,k}(-\delta\beta, \mp\delta\alpha) = \pm 2\Pi_{ij,k}\delta\beta\delta\alpha \qquad (22)$$

and some representative values are given in Table III.

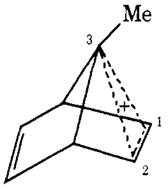
For the tropenylium cation (**3**), the interaction energy between an inductively electron donating substituent (+*I*, $-\delta\alpha$) and homoconjugate linkage is predicted to be positive (favorable) for the 1 and 3 isomers. For the 2 and 4 isomers, the interplay between bridge and substituent will be destabilizing (nevertheless, it should be noted that the overall energy change on +*I* substitution, irrespective of position, will be favorable, as a result of the first-order and diagonal second-order changes, which will be positive). Thus, the protonation of methyl- and phenylcyclooctatetraenes (**12**) leads to the 1-substituted homotropenylium cations (**13**),[27] although thermodynamic control was not established.[27]



12 **13**

R = Me, Ph

There is little evidence available on substituent effects in other homoaromatic systems. Brookhart, Lustgarten, and Winstein[28] have found that the equilibrium between **14** and **15** lies strongly in favor of the 2-methyl derivative (**15**). If we regard the system as a bishomocyclopropenium cation, then application of eq 22 leads to



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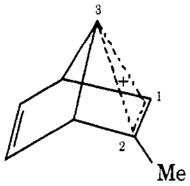

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$$E^2(-\delta\beta, -\delta\alpha) = 2(\Pi_{23,3} + \Pi_{13,3})\delta\alpha\delta\beta = 0.2962\delta\alpha\delta\beta$$

for **14** and

$$E^2(-\delta\beta, -\delta\alpha) = 2(\Pi_{23,2} + \Pi_{13,2})\delta\alpha\delta\beta = -0.1482\delta\alpha\delta\beta$$

for **15**. Thus the picture of **14** and **15** as perturbed cyclopropenium systems leads to a serious disagreement with experiment. This emphasizes anew that the distinction between homoconjugative and π-complex interactions are more than a matter of semantics.[2,29]

The two extremes of bishomocyclopropenium cation (**16**) and π-complex interaction (**17**) between cationic center and ethylene unit are shown below.

Obviously, the π complex (**17**) bears little resemblance to the usual description of a homoaromatic system, and in fact is sufficiently different from the HMO picture of π-electron systems to effectively preclude any treatments of **17** which are based on this method.[29]

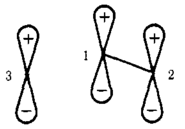
Nevertheless, theoretical treatments which can adequate-

Table II. $E^2{}_{ij,kl}$ Values for the Insertion of Two Homoconjugate Linkages

Parent system	Isomer	ij,kl	$E^2_{ij,kl}(\times 1/\delta\beta^2)^a$ (β)
1		12,12	0.2963
	1,2	12,23	−0.1481
2		12,12	0.4631
	1,2	12,23	−0.3135
	1,3	12,34	0.0820
3		12,12	0.5386
	1,2	12,23	−0.3785
	1,3	12,34	0.1452
	1,4	12,45	−0.0360
4		12,12	0.5809
	1,2	12,23	−0.4144
	1,3	12,34	0.1782
	1,4	12,45	−0.0797
	1,5	12,56	0.0254
5		12,12	0.6098
	1,2	12,23	−0.2955
	1,3	12,34	−0.0366
	1,4	12,45	0.1187
	1,5	12,56	−0.1831
6		12,12	0.4815
	1,2	12,23	−0.4074
	1,3	12,34	0.2593
	1,4	12,45	−0.1852

[a] See eq 21.

ly describe the interactions in π complexes[30] and experimental measurements[31] fully support a structure in which most of the charge density in systems such as **17**, is localized at C-1 and C-2. That **14** and **15** resemble the situation in **17**, with little or no contribution from **16**, follows from the geometrical requirements of the system, and considerable rehybridization of C-3 from sp^2 to sp^3 is expected.[4a,30]



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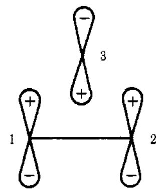

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Finally, we note that the occurrence of significant homoconjugate overlap in the absence of a simple methylene type bridge (quasicyclopropane unit) has yet to be demonstrated.[14]

3. **The Effect of the Homoconjugate Linkage on Charge Densities in Homoaromatic Molecules.** In this section we shall be concerned with the charge density differences ($\zeta_k{}^1$) brought about by the insertion of a homoconjugate linkage into the parent ion.[26] From eq 15 this is seen to be:

$$\zeta_k{}^1(-\delta\beta) = 2\Pi_{ij,k}\delta\beta \qquad (23)$$

Obviously, the results of the previous section may be interpreted in terms of just such an effect, and in fact the parallel between the expressions for the two quantities is complete (cf. eq 22 and 23 and Table III).

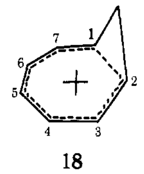
^{13}C- and, to a lesser extent, ^{1}H-NMR chemical shifts have proved to be a very sensitive probe of the charge densities of conjugated sp^2 carbon atoms.[32,33] It has been shown that the ^{13}C- and ^{1}H-NMR chemical shifts of the attached hydrogen are deshielded (to positive δ), when the carbon atom is positively charged. The ^{13}C- and ^{1}H-NMR chemical shifts of the homotropenylium (**18**)[17,21d,34] and 1,3-bishomotropenylium (**11**)[5e,21d] cations are reproduced in Table IV.

Table III. $E^2_{ij,k}$ and ζ^1_k Values for Homoaromatic Systems

Parent system	Isomer	ij,k	$E^2_{ij,k}(\mp\delta\alpha,-\delta\beta)(\times 1/\delta\alpha\delta\beta)^a$ (β) and $\zeta^1_k(-\delta\beta)(\times 1/\delta\beta)^{b,c}$
1	1	12,2	±0.1481
	2	12,3	∓0.2963
2	1	12,2	∓0.1262
	2	12,3	±0.1704
	3	12,4	∓0.0884
3	1	12,2	±0.1038
	2	12,3	∓0.1227
	3	12,4	±0.0737
	4	12,5	∓0.1097
4	1	12,2	∓0.0871
	2	12,3	±0.0968
	3	12,4	∓0.0643
	4	12,5	±0.0838
	5	12,6	∓0.0584
5	1	12,2	∓0.1875
	2	12,3	±0.1875
	3	12,4	∓0.0625
	4	12,5	±0.0625

[a] See eq 22. [b] Given by the upper sign in units of positive charge. Thus a + sign corresponds to carbonium character and a − sign denotes carbanion character. [c] See eq 23.

Table IV. ^{13}C- and ^{1}H-NMR Chemical Shifts of the Homotropenylium (18) and 1,3-Bishomotropenylium (11) Cations



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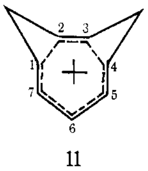

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		Chemical shifts, δ^a		
		^{13}C		^{1}H
Molecule	Position	Group A[c]	Group B[d]	Group C[e]
18	1,2	0.0	0.0	6.48
	3,7	31.5	23.1	8.39
	4,6	23.0	31.7	8.57
	5	22.5	22.3	8.27
		Group A[c]		Group E[f]
11	2,3	0.0[b]		7.00
	1,4	4.1[b]		7.18
	5,7	30.9		7.98
	6	46.4		9.06

[a] The ^{13}C-NMR values are quoted with the homoconjugate carbon atoms as reference. [b] Interchangeable values (assignment uncertain; see text). [c] Reference 21d. [d] Reference 17. [e] Reference 34. [f] Reference 5e.

As may be seen, there is some disagreement as to the correct assignment of the C-3,7 and C-4,6 resonances of **18**. The results of Oth and coworkers[17] (group B) are in good agreement with the predictions of eq 23 (Table III) (which also dovetails with the ^{1}H-NMR chemical shifts), and we have little doubt that their assignment is correct.

In the presence of bishomoconjugation, the summation in eq 15 gives rise to two terms (eq 23) for the perturbed charge densities ($\zeta_k{}^1(-\delta\beta)$) which in the case of **11** leads to:

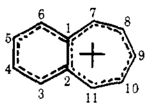
$$\zeta_1{}^1(-\delta\beta)(=\zeta_4{}^1) = 2\Pi_{12,1}\delta\beta + 2\Pi_{34,1}\delta\beta = 0.1775\delta\beta$$

$$\zeta_2{}^1(-\delta\beta)(=\zeta_3{}^1) = 2\Pi_{12,2}\delta\beta + 2\Pi_{34,2}\delta\beta = -0.0189\delta\beta$$

$$\zeta_5{}^1(-\delta\beta)(=\zeta_7{}^1) = 2\Pi_{12,5}\delta\beta + 2\Pi_{34,5}\delta\beta = -0.2324\delta\beta$$

$$\zeta_6{}^1(-\delta\beta) = 2\Pi_{12,6}\delta\beta + 2\Pi_{34,6}\delta\beta = 0.1474\delta\beta$$

Table V. E^1 and E^2 Values for the Insertion of a Homoconjugate Linkage into the Benzotropenylium Cation (**28**)



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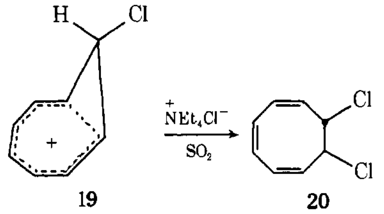
Position (ij)	$E^1(\times 1/\delta\beta)^a$ (β)	$E^2(\times 1/\delta\beta^2)^b$ (β)
1,2	−0.9791	0.2794
2,3	−1.1224	0.2980
3,4	−1.4322	0.2216
4,5	−1.2033	0.3039
1,7	−1.1004	0.3032
7,8	−1.3478	0.2742
8,9	−1.2581	0.2971

[a] See eq 16a. [b] See eq 16b.

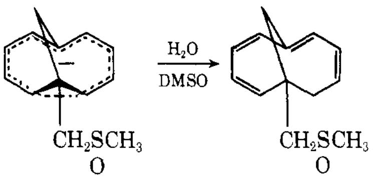
Again, these perturbed charge densities are in accord with the differences in the ^{13}C- and ^{1}H-NMR chemical shifts of the conjugated carbon atoms and their attached hydrogens. In the experimental measurement[21d] of the ^{13}C-NMR chemical shifts of **11**, it was not possible to unambiguously assign the C-2,3 and C-1,4 resonances, but from the perturbed charge densities calculated above, it appears that the assignment should be as it appears in Table IV (in accord with the PMR chemical shifts).[35]

Quenching experiments provide another way in which to test the predicted charge densities, as attack is expected to occur at the position of highest charge density.[6] It may be seen from Table III that in all cases the highest charge density is expected to occur at the carbons atoms comprising the homoconjugate linkage. Huisgen and coworkers[36] have reported that the collapse of the 8-chlorotropenylium cation (**19**) by nucleophilic attack of chloride ion does occur (stereospecifically) at the 1 position.



19 **20**

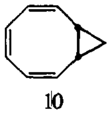
It has also been noted[37] that the 10π-electron homoaromatic **21** quenches in the same manner to give **22**.



21 **22**

Other experiments, which are less significant in the present context, also support this mode of attack on homoaromatic ions.[21a]

In sharp contrast stands the dianion (**23**) of *cis*-bicyclo[6.1.0]nonatriene (**10**) which has been formulated as the 10 π-electron homoaromatic **24**.[38] The methanol quench of the dianion leads to the bicyclooctadiene (**25**) in which, against previous experience, the cyclopropane ring is retained[60]. This, of course, is the quenching product which would be expected from **26**, and it may be that a substantial contribution from this structure should be included in the formulation of **23**. This would be in agreement with the small ring current indicated for **23** (as evidenced by the chemical shifts of the bridge protons).[39] As the chemical shifts of the ring protons show, however, the involvement of **24** cannot be disregarded.[4a,38] Nevertheless, it appears that in the case of **23** there is an insufficient donation of electron density into the cyclopropane unit to lead to the traditional "open" picture of homoaromaticity[4a,5e,11,14] (**24**), and under these conditions the PMO treatment of the atoms comprising the homoconjugate linkage (C1,C8) as a perturbed part of the π-electron system will be inappropriate.



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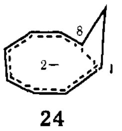

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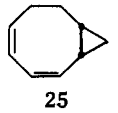

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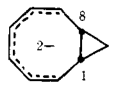

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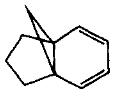
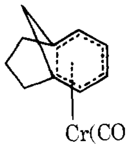
If indeed structure **26** makes a significant contribution to the ground state of **23**, then it may be that complexation with a metal atom which has a preference for 10π-electron ligands (as is found in the uranocenes[40]) will force an increased participation from structure **24**. This effect has been demonstrated for 6π systems by Vogel, Mills, and coworkers,[41] who showed that the norcaradiene hydrocarbon tricyclo[4.3.1.$0^{1,6}$]deca-2,4,-diene (**27a**) was converted into the homoaromatic (**27b**) by complexation with chromium tricarbonyl.



27a

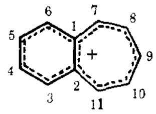


27b

Annelated Homoaromatic Systems

In this section we use the annelated aromatic system as reference point.[42,43]

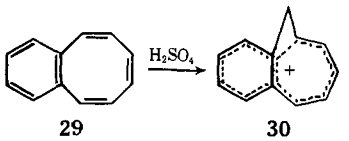
We shall illustrate the analysis by considering the homoaromatic derivatives of the benzotropenylium cation (**28**),[44] the E^1 and E^2 values of which are given in Table V (from eqs 16a and 16b); as may be seen, the energy differences arise primarily from the first-order term.



28

In dealing with such systems we might well expect that steric effects (which have played a surprisingly small part so far) will come to the fore in determining the relative stabilities of these molecules with respect to the position of the homoconjugate linkage. This should be particularly true of a homoconjugate linkage involving C-1 or C-2 where the necessary out-of-plane deformation is expected to be particularly difficult.

Thus, for the protonation of benzocyclooctatetraene (**29**) three homoconjugated benzotropenylium cations are possi-



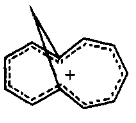
29 **30**

ble (the 1,7, 7,8, and 8,9 isomers). Surprisingly, however, Merk and Pettit[45] have shown that this reaction leads to **30**, which employs just this sort of sterically unfavorable 1,7 homoconjugation.

While this result is in accord with the analysis presented in Table V, it should be noted that thermodynamic control was not established for the above reaction.[45]

The 7,8-homoconjugated isomer is also known[23c] (prepared from the corresponding cyclopropyl alcohol), although it may be less stable than **30**.[46]

The 1,2-bridged benzotropenylium cation synthesized by Vogel and coworkers[47,48] is usually interpreted in terms of structure **31**, rather than **32**,[49] in common with the neutral counterpart which is best described by **33**, as opposed to **34**.[50]



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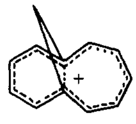

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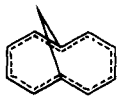

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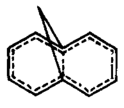


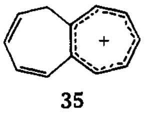
34

A 1,2-homoconjugate linkage leads to the smallest energy change for this system (**28**), and it is evident that even for a substantial value of $\delta\beta$ (reduction in the homoconjugate resonance integral), the gain in π-electron energy will not be too severe. The system is probably best described as a perturbed [11]annulenium cation (rather than a perturbed benzotropenylium cation).[49] Thus in this case it would be preferable to use the usual PMO approach[6] and starting with the aromatic monocycle consider the effect of a 1,6-transannular interaction. In this case $\delta\beta$ will be positive, and from eq 7 and 8 to second order the energy change will be given by $E^1 + E^2$ where

$$E^1(\delta\beta) = 2p_{ij}\delta\beta$$
$$E^2(\delta\beta) = \Pi_{ij,ij}\delta\beta^2 \qquad (24)$$

Thus we obtain[7] $E^1 + E^2$ values of $2 \times 0.1388\delta\beta + 0.4094\delta\beta^2$ and $2 \times 0.2\delta\beta + 0.3747\delta\beta^2$ for **32** and **34**, respectively; as expected, it may be seen that in the limit $\delta\beta \rightarrow 1$, the results from either starting point are very similar. That neither molecule apparently avails itself of this extra stabilization to any great extent is undoubtedly due to the particular steric requirements of these systems, together with the effective dispersal of charge density which is operative even in the absence of homoconjugation.

In their preparation of heptalene, Dauben and Bertelli[51] obtained the 1-heptalenium cation as the immediate precursor (the same product is obtained on protonation of heptalene[52]), to which they assigned the structure **35**.



35

An alternative formulation, however, could involve some 2,3-homoconjugation, and the NMR[51,53] and electronic[52] spectra do not appear to completely rule out a contribution from **36**. It would, of course, require the bridge flipping process (**36**) to explain the NMR spectrum, but some such conformational interchange is required anyway, in order to make the proposed structure[52] and the NMR[51,53] compatible. That this process would require a low energy of activation is in line with the behavior found for **18**[54] and **30**,[45] as the strain energy of achieving the conformation **36** would be high. Nevertheless, in the absence of more compelling evidence, the structure is probably best written in terms of **35**, which continues the nonoccurrence of unconstrained homoaromaticity in rings where the conjugation is over less than seven carbon atoms.

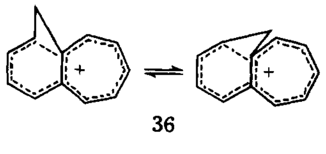


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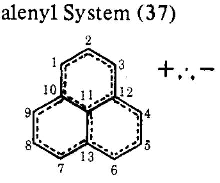
Table VI. E^1 and E^2 Values for the Insertion of a Homoconjugate Linkage into the Phenalenyl System (37)



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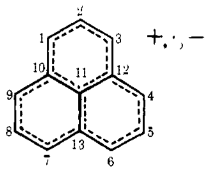
Position (ij)	$E^1(\times 1/\delta\beta)^a$ (β)	$E^2(\times 1/\delta\beta^2)^b$ (β)
1,2	−1.3407	0.2912
1,10	−1.1039	0.3161
10,11	−1.0532	0.2600

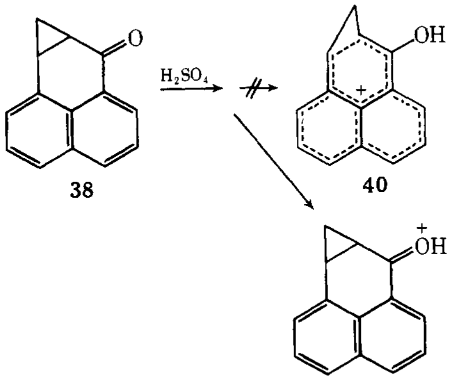
[a] See eq 16a. [b] See eq 16b.

Similar remarks apply to the phenalenyl system (**37**) where again the conjugation would have to be over a pseudo-six-membered ring, and it is for this reason we include it here. It should be noted, however, that the singular properties of this system result from the phenalenyl unit as a whole, rather than any single ring within the molecule.[55]



37

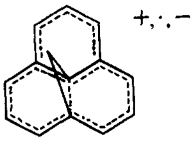
The E^1 and E^2 values (eq 16a and 16b)[56] for **37** are given in Table VI, and again it may be seen that first-order effects dominate the analysis. 1,2-Homoconjugation leads to the most unfavorable energy change (and thus the drive for homoaromatization will be greatest); however, protonation of the ketone **38**, apparently leads to **39** rather than **40**.[57] A final answer to the question of 1,2-homoconjugation in **37** must await the preparation of the unsubstituted derivative.[57]



38 **40** **39**

Homoconjugation across the 1,10 position has not been experimentally tested as yet, although a suitable skeleton would presumably arise (for the cation) by protonation of pleiadiene.[58]

The lowest E^1 value arises from 10,11-homoconjugation (**41**), and this system bears an obvious resemblance to the 1,6-methano[10]annulenes synthesized by Vogel;[59] whether or not the same weak transannular interaction will be preferred by **41** should be of great interest.[60]



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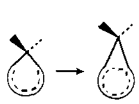
(8) See ref 6b.

(9) This is, of course, just the reverse of the usual PMO treatment of aromaticity in annulenes,[2] which considers the energy chan*ge o*n cyclization of the open chain analog.

(10) M. J. S. Dewar, *Rev. Mod. Phys.*, **35**, 586 (1963).

(11) The homoaromatization energy is a convenient concept, which has been implicit in much of the earlier work.[4] It will be used here to denote the energy change for the following process



A B

where A is assumed to be approximately planar and without homoconjugative interactions. Within this definition then, the homoaromatization energy is a measurable quantity, as A has been postulated[4] to be the transition state for the bridge flipping process observed in certain cases by NMR. It will obviously be (essentially) a sum of two opposing terms: the strain energy difference between A and B and the π-electron energy difference between A and B (with which we are concerned). In a homoantiaromatization process both terms will lead to an unfavorable energy change, and not surprisingly, no examples of such a conversion have been reported (see ref 5f and 12–14 for discussions of this point). Clearly we have adopted the Winstein picture of homoaromaticity with an "open" cyclopropane unit in which the atoms comprising the homoconjugate linkage may be treated as a perturbed part of the π-electron system.[4a,5e,14]

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(16) It should also be noted that a value of $\delta\beta \equiv 0$ is probably impossible for homoconjugate linkages. The most ideal case to date seems to be provided by the homotropenylium cation, for which $\delta\beta \simeq 0.27$ may be inferred from spectroscopic studies.[5e]

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(18) See ref 4b.

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(23) (a) It has been suggested[21d] that **11** may have the bridges transoid rather than cisoid (as pictured), and while this would not change the arguments we have used here, such a possibility seems unlikely on the basis of previous work which has shown the importance of p_π orbital alignment;[23b,c] (b) E. Vogel, *Pure Appl. Chem.*, **20**, 237 (1969); (c) H. A. Corver and R. F. Childs, *J. Am. Chem. Soc.*, **94**, 6201 (1972).

(24) The inductive stabilization of a π-electron carbonium ion by methyl substitution provides a good example, and Streitwieser[25] has recommended a value of -0.5β for $\delta\alpha$ at the site of the methyl substituent. Thus, conjugative and hyperconjugative effects are excluded from the treatment. Nevertheless, even where such effects are expected to be operative, they do not appear to upset the qualitative predictions of the treatment.

(25) Reference 6b, Chapters 5 and 11.

(26) Note that neutral homoaromatics are specifically excluded from this discussion as the π systems within such molecules are even alternant "hydrocarbons" (irrespective of the amount of homoconjugation), for which the charge densities (ζ_i) and the $\Pi_{ij,k}$ are always zero.

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Molecular Orbital Studies of Electron Donor-Acceptor Complexes. I. Carbonyl Cyanide-ROR and Tetracyanoethylene-ROR Complexes

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Abstract: Ab initio molecular orbital methods are used to study the ground and the charge-transfer states of the weak electron donor-acceptor complexes: carbonyl cyanide-ROR and tetracyanoethylene-ROR where water is used in most calculations as a model for the ether. Modes of approach of the water upon the acceptor molecules were investigated and results of geometries and interaction energies are in reasonable agreement with experiment. The decomposition of interaction energies into components and the comparison with simple electrostatic models indicate that for the complexes studied, the electrostatic energy is the predominant term in their stabilization.

I. Introduction

The origin of the attractive forces responsible for the intermolecular binding of two molecules has been sought for some time. Although the majority of effort has been directed toward the understanding of hydrogen-bonded systems,[1] another area of current interest is that of so-called "charge-transfer" complexes.[2] The ground state wave function for such a complex between a donor molecule D and an acceptor molecule A is traditionally expressed as

$$\Psi_{DA}{}^{GS} \approx a\psi(D, A) + b\psi(D^+-A^-)$$

a sum of a no-bond resonance structure $\psi(D,A)$ and a dative resonance structure $\psi(D^+-A^-)$ corresponding to an ionic plus a covalent bond. The amount of charge transfer is judged by the relative values of the coefficients a and b: the larger b, the greater the contribution of $\psi(D^+-A^-)$ and hence more charge transfer. A "charge-transfer" band is sometimes seen in the electronic absorption spectrum arising from the transition from the ground state to the charge-transfer state with approximate wave function

$$\Psi_{DA}{}^{CT} \approx -b\psi(D, A) + a\psi(D^+-A^-)$$

An example of such a band is apparent in the spectrum of the much-studied benzene-iodine system. In the charge-transfer state the predominant resonance structure is the dative one in which an electron has been transferred from the electron donor to the acceptor.

The amount of charge transfer in the ground state of both strong and weak "charge-transfer" complexes has received much attention in the chemical literature. Although a large charge-transfer effect is usually conceded for strong complexes, there has been considerable discussion concerning the origin of the attractive forces in weak "charge-transfer" complexes. Through the efforts of many workers (e.g., Hanna, who showed that the quadrupole-induced dipole forces are of considerable importance in complexes between benzene and halogens[3]), electrostatic forces are presently believed to be the predominant factor in the intermolecular binding in weak "charge-transfer" complexes. For this reason the term "charge-transfer complex" is in disfavor with the preferred expression being "electron donor-acceptor complex".[2a]

In the present work we report the results of an ab initio molecular orbital study of two weak "charge-transfer" complexes in an attempt to further elucidate the intermolecular binding in these systems. The first system, for which a preliminary report has appeared previously,[4] is carbonyl cyanide-ROR, an example of an nπ complex. The second is another nπ complex, tetracyanoethylene-ROR. In most of our calculations we employ water as a model for the ether moiety in order to make the complexes of a size amenable to ab initio methods at a reasonable computational expense.[5] Another reason for the choice of the carbonyl cyanide-ROR