Extended Valence Bond Theory, Aromaticity, and the Woodward–Hoffmann Rules

W. J. van der Hart,* J. J. C. Mulder, and L. J. Oosterhoff

Contribution from the Department of Theoretical Organic Chemistry, University of Leiden, Leiden, The Netherlands. *Received December 21, 1971*

Abstract: Aromaticity and the Woodward–Hoffmann rules are discussed using an extended valence bond method in which the Heitler–London functions for the bonds are replaced by general two-electron functions. Problems raised by the formation and stability of the benzene valence isomers prismane, Dewar benzene, and benzvalene, which remain unsettled in other treatments, find their natural solution in the present formulation. It is shown that previous discussions by van der Lugt and Oosterhoff and by Mulder and Oosterhoff are special examples of the present approach.

1. Introduction

The Woodward–Hoffmann rules[1] can be obtained in a simple and general way by requiring the transition state of an allowed reaction to be aromatic. This method has been used especially by Dewar[2] and Zimmerman[3] and is also essential in the papers on permutation symmetry control by Mulder and Oosterhoff.[4]

In discussing relative stabilities of transition states we do not avoid the controversial term aromaticity. We realize that for a long period the word aromatic was used to summarize the *chemical* behavior of a class of compounds and that it was this behavior for which Hückel[5] suggested an explanation in terms of his $4n + 2$ rule. Fundamental in Hückel's reasoning is the large energy gap between ground state and excited state(s) in a ring with $4n + 2$ electrons which contrasts the small separation in a ring with $4n$ electrons. Present day (ab)usage of the words aromatic and antiaromatic concentrates on the energetic stability of the ground state. The connection with Hückel's original reasoning becomes clear if we remember the explanation given previously[4,6] for the opposite behavior of photochemical and thermal reactions: in an aromatic transition state (thermally allowed reaction path) a large gap exists between the electronic ground state and the next excited state whereas in an antiaromatic transition state (forbidden reaction path) ground state and excited state(s) come close together. In this paper the first general derivation of the $4n + 2$ rule is given (eq 1).

Aromaticity rules are generally thought to be readily derived from molecular orbital theory. Therefore it is not surprising that the Woodward–Hoffmann rules are usually obtained within the MO formalism. Despite the apparent success of MO theory there are nevertheless several reasons why a valence bond approach is more appropriate for the problem considered here. First of all, pericyclic reactions can often be described as an isomerization from one valence structure to another.[7] This point, which is closely connected with the VB method, is difficult to envisage in MO theory. A second reason is the fact that in the VB method states instead of one-electron orbitals are considered. Therefore, the joint influence of all electrons together is effective from the beginning whereas in the MO discussion this essential factor is introduced in a second step when the molecular orbitals are combined to state functions. These two points illustrate that the VB method is a more direct tool in the search for the fundamental factors determining aromaticity and the Woodward–Hoffmann rules.

According to a VB approximation with neglect of "long-bond structures" the resonance energy of $2n$-membered rings is

$$\{-3n/(2^n + 2)\}J$$

where J is the exchange integral, which is assumed to be negative. This result does not agree with Hückel's rule and thus shows that aromaticity and consequently the Woodward–Hoffmann rules should be discussed in terms of a VB method which goes beyond the classical assumptions. In their calculations with orthogonal atomic orbitals van der Lugt and Oosterhoff (Lu–O)[6] had to include completely ionic structures with alternating positive and negative charges. Mulder and Oosterhoff (Mu–O)[4] showed that cyclic permutations of all electrons are essential when the atomic orbitals are nonorthogonal but ionic structures are neglected.

In the present paper we will show that a generalized valence bond method can be formulated which contains both the Lu–O and Mu–O results as special examples.

Before starting our analysis we would like to point out two important applications of the present treatment.

First the presence of more than one ring is handled in a straightforward manner. This means that the valence isomerizations of benzene follow directly. For example, the forbidden character of the conversion of prismane to benzene follows immediately from the general rule formulated in eq 7.

Secondly odd-membered ionic as well as neutral systems are treated in a completely analogous way and

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[1] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Academic Press, Weinheim Bergstr., Germany, 1970.

[2] M. J. S. Dewar, *Tetrahedron, Suppl.*, **8**, Part I, 75 (1966); M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

[3] H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966).

[4] J. J. C. Mulder and L. J. Oosterhoff, *Chem. Commun.*, 305, 308 (1970); J. J. C. Mulder, Thesis, Leiden, 1970.

[5] E. Hückel, *Z. Phys.*, **70**, 204 (1931).

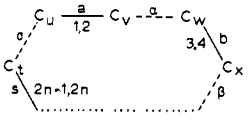
[6] W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968); W. Th. A. M. van der Lugt, Thesis, Leiden, 1968; W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

[7] M. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, **34**, 614 (1938).

the results agree with what is known about these cases.

2. Monocyclic Systems

We first consider monocyclic systems. In the case of Woodward–Hoffmann rules this implies that we discuss the transition state of reactions such as the interconversion of hexatriene and cyclohexadiene. A general reaction of this type can be described as a cyclic isomerization in which the bonds a, b, . . ., s in A



A

are replaced by the bonds α, β, . . ., σ. The reaction will be allowed if the ring system pictured in A is aromatic. In our discussion of this problem we will take the wave functions for the structures with bonds a, b, . . ., s and with bonds α, β, . . ., σ to be

$$\Psi_{\mathrm{I}} = \{2^n/(2n)!\}^{1/2}\sum_P{}'\epsilon_{\mathrm{P}}Pa(1, 2)b(3, 4)\ldots s(2n-1, 2n) \times [1, 2][3, 4]\ldots[2n-1, 2n]$$

$$\Psi_{\mathrm{II}} = \{2^n/(2n)!\}^{1/2}\sum_P{}'\epsilon_{\mathrm{P}}P\alpha(3, 2)\beta(5, 4)\ldots\sigma(1, 2n) \times [3, 2][5, 4]\ldots[1, 2n]$$

The wave functions without the antisymmetrizer will be written ϕ_1^{I} and ϕ_1^{II}; the space parts of ϕ_1^{I} and ϕ_1^{II} are f_1^{I} and f_1^{II}, respectively. The summation over P includes all $(2n)!/2^n$ permutations which interchange electrons between different bonds, $\epsilon_{\mathrm{P}} = \pm 1$ depending on the parity of the permutation and $[i,j]$ stands for the singlet spin function $\{\alpha_i\beta_j - \beta_i\alpha_j\}/\sqrt{2}$. It should be noted that ψ_{I} and ψ_{II} are not identical with the usual valence bond wave functions; $a(1, 2)$, say, is now a general two-electron function, which may contain both covalent and ionic terms.

The resonance energy of the ring system will be defined in the classical way as the energy lowering due to the mixing of ψ_{I} and ψ_{II}. Depending on the sign of the Hamilton matrix element $H_{\mathrm{I,II}}$, the ground state wave function is either $(\psi_{\mathrm{I}} + \psi_{\mathrm{II}})/(2S_{\mathrm{I,I}} + 2S_{\mathrm{I,II}})^{1/2}$ or $(\psi_{\mathrm{I}} - \psi_{\mathrm{II}})/(2S_{\mathrm{I,I}} - 2S_{\mathrm{I,II}})^{1/2}$, where $S_{i,j}$ is the overlap matrix element. In the first case the resonance energy is

$$\frac{H_{\mathrm{I,I}}}{S_{\mathrm{I,I}}} - \frac{\{2H_{\mathrm{I,I}} + 2H_{\mathrm{I,II}}\}}{\{2S_{\mathrm{I,I}} + 2S_{\mathrm{I,II}}\}} = \frac{H_{\mathrm{I,I}}S_{\mathrm{I,II}} - H_{\mathrm{I,II}}S_{\mathrm{I,I}}}{S_{\mathrm{I,I}}\{S_{\mathrm{I,I}} + S_{\mathrm{I,II}}\}}$$

whereas the second possibility yields

$$\frac{H_{\mathrm{I,I}}}{S_{\mathrm{I,I}}} - \frac{\{2H_{\mathrm{I,I}} - 2H_{\mathrm{I,II}}\}}{\{2S_{\mathrm{I,I}} - 2S_{\mathrm{I,II}}\}} = \frac{H_{\mathrm{I,II}}S_{\mathrm{I,I}} - H_{\mathrm{I,I}}S_{\mathrm{I,II}}}{S_{\mathrm{I,I}}\{S_{\mathrm{I,I}} - S_{\mathrm{I,II}}\}}$$

Roughly speaking, $H_{\mathrm{I,I}}$ and $S_{\mathrm{I,I}}$ vary linearly with the number of atoms $2n$ so the aromatic or nonaromatic character of the ring system is determined by the factors $H_{\mathrm{I,II}}$ and $S_{\mathrm{I,II}}$. Therefore we consider the general matrix element

$$\begin{aligned}\langle\Psi_{\mathrm{I}}|\Omega|\Psi_{\mathrm{II}}\rangle = {} & \{2^n/(2n)!\}\langle\sum_R{}'\epsilon_{\mathrm{R}}Ra(1, 2)b(3,4)\ldots(2n-1, 2n) \times \\ & [1, 2][3, 4]\ldots[2n-1, 2n|\Omega|\sum_P{}'\epsilon_{\mathrm{P}}P\alpha(3, 2) \times \\ & \beta(5, 4)\ldots\sigma(1, 2n)[3, 2][5, 4]\ldots[1, 2n]\rangle = \\ & \langle a(1, 2)b(3, 4)\ldots s(2n-1, 2n) \times \\ & [1, 2][3, 4]\ldots[2n-1, 2n]|\Omega|\sum_P{}'\epsilon_{\mathrm{P}}P\alpha(3, 2) \times \\ & \beta(5, 4)\ldots\sigma(1, 2n)[3, 2][5, 4]\ldots[1, 2n]\rangle\end{aligned}$$

In the evaluation of this matrix element we consider nearest-neighbor interactions only (see the Appendix for a further discussion of this point). Then it follows immediately that only those permutations need to be considered which yield a function $\phi_i^{\mathrm{II}} = P_i\phi_1^{\mathrm{II}}$ in which the electron numbers of the bonds are identical with two of the electron numbers of the neighboring bonds in ϕ_1^{I}. Thus, *e.g.*, the electron numbers 1 and 2 which are in a in ϕ_1^{I} should either be in α or in σ in ϕ_i^{II} (see A). In the same way 3 and 4 should either be in α or in β, etc.

The relevant permutations can now be divided into three groups.

(1) Consider a function $\phi_i^{\mathrm{II}} = P\phi_1^{\mathrm{II}}$ in which α has one electron number from bond a and one from bond b, *e.g.*, $\alpha(3, 2)$. The electron number 1 should be in σ and number 4 in β. The second electron number of β should be taken from bond c in ϕ_1^{I}, so we have $\beta(5, 4)$ or $\beta(6, 4)$, etc. Repeating this process around the ring system we will find that each function in ϕ_i^{II} has one electron number from both neighboring bonds of ϕ_1^{I}. Since we have n pairs of electrons, this distribution can be realized in 2^n different ways. We thus obtain 2^n different permutations, including the identity, which are interconnected by transpositions of electron numbers which are in the same bond in ϕ_1^{I}. From the latter property it follows that all of these 2^n permutations yield identical contributions to the matrix element.

(2) In the second type of permutation α has both electron numbers of bond a in ϕ_1^{I}, so we have $\alpha(1, 2)$. It follows immediately that β has both electron numbers of bond b: $\beta(3, 4)$, etc. We thus have only one possible permutation of this type, yielding

$$\phi_2^{\mathrm{II}} = \alpha(1, 2)\beta(3, 4)\ldots\sigma(2n-1, 2n) \times [1, 2][3, 4]\ldots[2n-1, 2n]$$

which is obtained from ϕ_1^{II} by a cyclic permutation of half the total number of electrons, so the parity is $(-1)^{n-1}$.

(3) In the same way we obtain a contribution from

$$\phi_3^{\mathrm{II}} = \alpha(3, 4)\beta(5, 6)\ldots\sigma(1, 2)[3, 4][5, 6]\ldots[1, 2]$$

where now the electron numbers of α and bond b, β and bond c, etc., are identical. $\Omega_{\mathrm{I,II}}$ then becomes

$$\langle\Psi_{\mathrm{I}}|\Omega|\Psi_{\mathrm{II}}\rangle = 2^n\langle\phi_1^{\mathrm{I}}|\Omega|\phi_1^{\mathrm{II}}\rangle + (-1)^{n-1}\{\langle\phi_1^{\mathrm{I}}|\Omega|\phi_2^{\mathrm{II}}\rangle + \langle\phi_1^{\mathrm{I}}|\Omega|\phi_3^{\mathrm{II}}\rangle\}$$

For spin-independent operators the spin factors can be removed by application of Pauling's rules. This yields

$$\langle \Psi_{\mathrm{I}}|\Omega|\Psi_{\mathrm{II}}\rangle = 2\langle f_1{}^{\mathrm{I}}|\Omega|f_1{}^{\mathrm{II}}\rangle + (-1)^{n-1}\{\langle f_1{}^{\mathrm{I}}|\Omega|f_2{}^{\mathrm{II}}\rangle + \langle f_1{}^{\mathrm{I}}|\Omega|f_3{}^{\mathrm{II}}\rangle\} \quad (1)$$

where $f_1{}^{\mathrm{I}}$, say, is the space part of $\phi_1{}^{\mathrm{I}}$.

It follows from eq 1 that the magnitude of the matrix element is strongly dependent on the value of n. When all three integrals on the right-hand side have equal signs, then $\Omega_{\mathrm{I,II}}$ has the form A + B if $n - 1$ is even and A − B if $n - 1$ is odd. This alternation in the magnitude of $\Omega_{\mathrm{I,II}}$ is reversed when the sign of the second and third integral is opposite to the sign of the first integral. On substitution in the formula for the resonance energy these two cases should just give the aromaticity rules for normal and Möbius ring systems, respectively. We will show the correctness of these assumptions about the signs of the integrals by comparison with the Lu–O and Mu–O treatments. This comparison will be done by considering the overlap matrix element $S_{\mathrm{I,II}}$ (one could also use $H_{\mathrm{I,II}}$ but then the discussion is somewhat more complex).

2.1. Calculations with Orthogonal Atomic Orbitals. We assume the two-electron bond functions to be calculated in a basis of two orthogonal atomic oribtals. Then the bond functions may be written

$$a(1, 2) = \mu_{\mathrm{a}}(u_1v_2 + v_1u_2)/\sqrt{2} + \nu_{\mathrm{a}}(u_1u_2 + v_1v_2)/\sqrt{2}$$

$$\alpha(1, 2) = \mu_{\alpha}(v_1w_2 + w_1v_2)/\sqrt{2} + \nu_{\alpha}(v_1v_2 + w_1w_2)/\sqrt{2}$$

$$b(1, 2) = \mu_{\mathrm{b}}(w_1x_2 + x_1w_2)/\sqrt{2} + \nu_{\mathrm{b}}(w_1w_2 + x_1x_2)/\sqrt{2}$$

etc. Here, u, v, w, and x are the atomic orbitals for the atoms C_u, C_v, C_w, and C_x (see A) and μ_{a} and ν_{a}, say, are the coefficients of the covalent and ionic terms in $a(1, 2)$.

We first consider the second integral in $S_{\mathrm{I,II}}$. This can be written

$$\langle f_1{}^{\mathrm{I}}|f_2{}^{\mathrm{II}}\rangle = \langle a(1, 2)|\alpha(1, 2)\rangle\langle b(3, 4)|\beta(3, 4)\rangle \ldots$$

Due to the neglect of atomic orbital overlap, $\langle a(1, 2)|\cdot \alpha(1, 2)\rangle$ is determined by the $C_u{}^+$–$C_v{}^-$ and $C_v{}^-$–$C_w{}^+$ terms in a and α, respectively, so

$$\langle a(1, 2)|\alpha(1, 2)\rangle = (\nu_{\mathrm{a}}\nu_{\alpha}/2)\langle v_1v_2|v_1v_2\rangle = \nu_{\mathrm{a}}\nu_{\alpha}/2$$

which yields

$$\langle f_1{}^{\mathrm{I}}|f_2{}^{\mathrm{II}}\rangle = \{\sqrt{2}\}^{-2n}\prod_{k=1}^{2n}\nu_k$$

where k numbers the bond functions in both ψ_{I} and ψ_{II}.

It follows that $\langle f_1{}^{\mathrm{I}}|f_2{}^{\mathrm{II}}\rangle$ depends on the completely ionic contributions to ψ_{I} and ψ_{II} having an alternating charge distribution with the negative charge on the atoms C_t, C_v, C_x .... The same result is obtained for $\langle f_1{}^{\mathrm{I}}|f_3{}^{\mathrm{II}}\rangle$ but now the atoms C_u, C_w, ... carry the negative charge. In $\langle f_1{}^{\mathrm{I}}|f_1{}^{\mathrm{II}}\rangle$, $\alpha(1, 2)$ shares one electron with both bond a and b, so this integral depends on the covalent contributions to ψ_{I} and ψ_{II}. It follows that

$$\langle f_1{}^{\mathrm{I}}|f_1{}^{\mathrm{II}}\rangle = \{\sqrt{2}\}^{-2n}\prod_{k=1}^{2n}\mu_k$$

We thus obtain

$$\langle \Psi_{\mathrm{I}}|\Psi_{\mathrm{II}}\rangle = 2^{-n+1}\left\{\prod_{k=1}^{2n}\mu_k + (-1)^{n-1}\prod_{k=1}^{2n}\nu_k\right\}$$

For normal ring systems the atomic orbitals can be chosen that all β values are negative (corresponding to positive overlap integrals in calculations without neglect of overlap). Then μ and ν have equal signs for each bond. In the case of Möbius ring systems, however, there remains one positive β value (negative overlap integral). For this bond μ and ν have opposite signs. We can take account of this difference by assuming μ and ν to be the values for a bond with a negative β value and correcting the sign by introduction of a factor $(-1)^r$ with r being the number of positive β values (negative overlap integrals). This yields as our final formula

$$\langle \Psi_{\mathrm{I}}|\Psi_{\mathrm{II}}\rangle = 2^{-n+1}\left\{\prod_{k=1}^{2n}\mu_k + (-1)^{r+n-1}\prod_{k=1}^{2n}\nu_k\right\} \quad (2)$$

This result confirms the interpretation of eq 1 given above. Moreover, it is in agreement with an observation made by van der Lugt from the Lu–O calculations.[8] According to van der Lugt the difference in the total energies of the transition states for the allowed and forbidden reaction pathways is caused by terms involving the completely ionic valence bond structures having an alternating charge distribution. This is just the same result as expressed by eq 2. If polar structures are neglected as in the usual valence bond method, eq 2 reduces to the first term only. This explains the failure of classical VB calculations in predicting aromaticity and the Woodward–Hoffmann rules.

2.2 Calculations with Nonorthogonal Atomic Orbitals. In order to compare our results with the Mu–O treatment, we neglect ionic contributions but include nearest-neighbor atomic overlap integrals. In this case the bond functions are

$$a(1, 2) = (u_1v_2 + v_1u_2)/(2 + 2S_{uv}{}^2)^{1/2}$$

$$\alpha(1, 2) = (v_1w_2 + w_1v_2)/(2 + 2S_{vw}{}^2)^{1/2}$$

$$b(1, 2) = (w_1x_2 + x_1w_2)/(2 + 2S_{xw}{}^2)^{1/2}$$

The major contribution to $\langle f_1{}^{\mathrm{I}}|f_1{}^{\mathrm{II}}\rangle$ is the usual valence bond result which does not predict aromaticity. In the present case there are some additional terms due to the inclusion of atomic orbital overlap. It can easily be shown, *e.g.*, by integrating the product of $f_1{}^{\mathrm{I}}$ and $f_1{}^{\mathrm{II}}$ over the electron numbers 1, 2, and 4, that the additional terms are proportional to the squares of the atomic orbital overlap integrals. Consequently, they do not differentiate between normal and Möbius ring systems and are thus also unable to predict aromaticity. $\langle f_1{}^{\mathrm{I}}|f_2{}^{\mathrm{II}}\rangle$ and $\langle f_1{}^{\mathrm{I}}|f_3{}^{\mathrm{II}}\rangle$ are products of integrals such as

$$\langle a(1, 2)|\alpha(1, 2)\rangle = 2S_{uv}S_{vw}/\sqrt{(2 + 2S_{uv}{}^2)(2 + 2S_{vw}{}^2)}$$

which yields

$$\langle f_1{}^{\mathrm{I}}|f_2{}^{\mathrm{II}}\rangle = \langle f_1{}^{\mathrm{I}}|f_3{}^{\mathrm{II}}\rangle = \prod_{k=1}^{2n} S_k\Big/\sqrt{1 + S_k{}^2}$$

where S_k is the overlap integral between the atomic orbitals of bond k. The product of all overlap integrals in this expression has opposite signs for normal and Möbius ring systems. This point can be made

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(8) W. Th. A. M. van derLugt, personal communication.

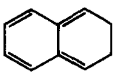
to come out more explicitly by writing

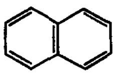
$$\langle f_1^{\mathrm{I}}|f_2^{\mathrm{II}}\rangle = \langle f_1^{\mathrm{I}}|f_3^{\mathrm{II}}\rangle = (-1)^r\prod_{k=1}^{2n}|S_k|\Big/\sqrt{1 + S_k^2}$$

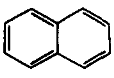
where r is the number of negative overlap integrals as before. These results again confirm the interpretation of eq 1. In the present approximation aromaticity is determined by the balance between the usual valence bond result with some additional terms proportional to the squares of the overlap integrals and a term which depends on the product of all overlap integrals. This is precisely the same result as obtained by Mu–O for their discussion of the role of cyclic permutations in valence bond calculations with inclusions of overlap.

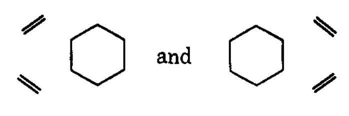
3. Polycyclic Systems

In the case of polycyclic systems, *e.g.*, naphthalene and azulene, we have the possibility of more than two Kékulé structures. *E.g.*, for naphthalene the structures are I, II, and III. The interaction between I and II and between II and III is determined by the superposition diagrams

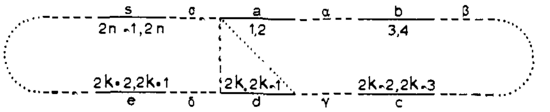

I


II


III



In this case the matrix elements depend largely on the separate rings in the superposition diagram. In correspondence with the previous section it follows that the interaction will be large if the separate rings are aromatic. The interaction between I and III is much more difficult to handle. The general superposition diagram for interactions of this kind is given by B.



B

The extra bond now introduces an essentially non-negligible, non-nearest-neighbor interaction. The non-nearest-neighbor interactions are of two types; they may split the system into two even-membered rings (dashed line in B) or into two odd-membered rings (dotted line in B). In the first case the number of bonds on the perimeter participating in the right ring is $2k - 1$, in the second case this number is $2k - 2$. The numbers in B represent the electron distribution in ϕ_1^{I} as before.

In order to obtain a contribution from the additional interaction, we must consider cyclic permutations of the electron numbers of all bonds participating in either the left or the right ring (and products of these permutations). The space parts of the functions ϕ_j^{II} which we choose to represent the different types of relevant permutations, this permutation in cycle notation, its parity and spin factor and the number of permutations of each kind are collected in Table I. The con-

Table I. Additional Permutations for Polycyclic Systems

Permutation	$P_if_1^{\mathrm{II}}$	ϵ_{p}	Spin factor	No. of permutations
$(1, 2k)$	$f_4 = \alpha(3, 2)\beta(5, 4)\ldots\gamma(2k - 1, 2k - 2)\delta(2k + 1, 1)\ldots\sigma(2k, 2n)$	-1	$-2^{-(n-1)}$	2^n
$(2k, 2k + 2,\ldots, 2n)$	$f_5 = \alpha(3, 2)\beta(5, 4)\ldots\gamma(2k - 1, 2k - 2)\delta(2k + 1, 2k + 2)\ldots\sigma(1, 2k)$	$(-1)^{n-k}$	$2^{-(k-1)}$	2^k
$(1, 2n - 1,\ldots,2k + 1)$	$f_6 = \alpha(3, 2)\beta(5, 4)\ldots\gamma(2k - 1, 2k - 2)\delta(1, 2k)\ldots\sigma(2n - 1, 2n)$	$(-1)^{n-k}$	$2^{-(k-1)}$	2^k
$(2k - 1, 2k - 3,\ldots,1)$	$f_7 = \alpha(1\ \ 2)\beta(3, 4)\ldots\gamma(2k - 3, 2k - 2)\delta(2k + 1, 2k)\ldots\sigma(2k - 1, 2n)$	$(-1)^{k-1}$	$2^{-(n-k)}$	2^{n-k+1}
$(2, 4,\ldots,2k)$	$f_8 = \alpha(3, 4)\beta(5, 6)\ldots\gamma(2k - 1, 2k)\delta(2k + 1, 2)\ldots\sigma(1, 2n)$	$(-1)^{k-1}$	$2^{-(n-k)}$	2^{n-k+1}
$(2k, 2k + 2,\ldots,2n)(2k - 1, 2k - 3,\ldots,1)$	$f_9 = \alpha(1, 2)\beta(3, 4)\ldots\gamma(2k - 3, 2k - 2)\delta(2k + 1, 2k + 2)\ldots\sigma(2k - 1, 2k)$	$(-1)^{n-1}$	1	1
$(1, 2n - 1,\ldots,2k + 1)(2, 4,\ldots,2k)$	$f_{10} = \alpha(3, 4)\beta(5, 6)\ldots\gamma(2k - 1, 2k)\delta(1, 2)\ldots\sigma(2n - 1, 2n)$	$(-1)^{n-1}$	1	1
$(1, 2k - 1)$	$g_4 = \alpha(3, 2)\beta(5, 4)\ldots\gamma(1, 2k - 2)\delta(2k + 1, 2k)\ldots\sigma(2k - 1, 2n)$	-1	$2^{-(n-2)}$	2^n
$(2k, 2k + 2,\ldots,2n)$	$g_5 = \alpha(3, 2)\beta(5, 4)\ldots\gamma(2k - 1, 2k - 2)\delta(2k + 1, 2k + 2)\ldots\sigma(1, 2k)$	$(-1)^{n-k}$	$2^{-(k-1)}$	2^k
$(1, 2n - 1,\ldots,2k - 1)$	$g_6 = \alpha(3, 2)\beta(5, 4)\ldots\gamma(1, 2k - 2)\delta(2k - 1, 2k)\ldots\sigma(2n - 1, 2n)$	$(-1)^{n-k+1}$	$2^{-(k-2)}$	2^{k-1}
$(2k - 1, 2k - 3,\ldots,1)$	$g_7 = \alpha(1, 2)\beta(3, 4)\ldots\gamma(2k - 3, 2k - 2)\delta(2k + 1, 2k)\ldots\sigma(2k - 1, 2n)$	$(-1)^{k-1}$	$2^{-(n-k)}$	2^{n-k+1}
$(2, 4,\ldots,2k - 2)$	$g_8 = \alpha(3, 4)\beta(5, 6)\ldots\gamma(2k - 1, 2)\delta(2k + 1, 2k)\ldots\sigma(1, 2n)$	$(-1)^{k-2}$	$2^{-(n-k+1)}$	2^{n-k+2}
$(2k, 2k + 2,\ldots,2n)(2k - 1, 2k - 3,\ldots,1)$	$g_9 = \alpha(1, 2)\beta(3, 4)\ldots\gamma(2k - 3, 2k - 2)\delta(2k + 1, 2k + 2)\ldots\sigma(2k - 1, 2k)$	$(-1)^{n-1}$	1	1
$(1, 2n - 1,\ldots,2k - 1)(2, 4,\ldots,2k - 2)$	$g_{10} = \alpha(3, 4)\beta(5, 6)\ldots\gamma(1, 2)\delta(2k - 1, 2k)\ldots\sigma(2n - 1, 2n)$	$(-1)^{n-1}$	1	1
$(2k, 2k + 2,\ldots,2n)(1, 2k - 1)$	$g_{11} = \alpha(3, 2)\beta(5, 4)\ldots\gamma(1, 2k - 2)\delta(2k + 1, 2k + 2)\ldots\sigma(2k - 1, 2k)$	$(-1)^{n-k+1}$	$2^{-(k-2)}$	2^{k-1}
$(2, 4,\ldots,2k - 2)(1, 2k - 1)$	$g_{12} = \alpha(3, 4)\beta(5, 6)\ldots\gamma(1, 2)\delta(2k + 1, 2k)\ldots\sigma(2k - 1, 2n)$	$(-1)^{k-1}$	$2^{-(n-k)}$	2^{n-k+1}
$(2, 4,\ldots,2k - 2)(2k, 2k + 2,\ldots,2n)$	$g_{13} = \alpha(3, 4)\beta(5, 6)\ldots\gamma(2k - 1, 2)\delta(2k + 1, 2k + 2)\ldots\sigma(1, 2k)$	$(-1)^{n-2}$	2^{-1}	2^2
$(2, 4,\ldots,2k - 2)(2k, 2k + 2,\ldots,2n)(1, 2k - 1)$	$g_{14} = \alpha(3, 4)\beta(5, 6)\ldots\gamma(1, 2)\delta(2k + 1, 2k + 2)\ldots\sigma(2k - 1, 2k)$	$(-1)^{n-1}$	1	1

tribution to $\Omega_{\mathrm{I,II}}$ for two even-membered rings is

$$2\langle f_1{}^{\mathrm{I}}|\Omega|f_4{}^{\mathrm{II}}\rangle + 2(-1)^{n-k}\{\langle f_1{}^{\mathrm{I}}|\Omega|f_5{}^{\mathrm{II}}\rangle + \langle f_1{}^{\mathrm{I}}|\Omega|f_6{}^{\mathrm{II}}\rangle\} + 2(-1)^{k-1}\{\langle f_1{}^{\mathrm{I}}|\Omega|f_7{}^{\mathrm{II}}\rangle + \langle f_1{}^{\mathrm{I}}|\Omega|f_8{}^{\mathrm{II}}\rangle\} + (-1)^{n-1}\{\langle f_1{}^{\mathrm{I}}|\Omega|f_9{}^{\mathrm{II}}\rangle + \langle f_1{}^{\mathrm{I}}|\Omega|f_{10}{}^{\mathrm{II}}\rangle\} \quad (3)$$

and for two odd-membered rings it is

$$-4\langle f_1{}^{\mathrm{I}}|\Omega|g_4{}^{\mathrm{II}}\rangle + 2(-1)^{n-k}\{\langle f_1{}^{\mathrm{I}}|\Omega|g_5{}^{\mathrm{II}}\rangle - \langle f_1{}^{\mathrm{I}}|\Omega|g_6{}^{\mathrm{II}}\rangle - \langle f_1{}^{\mathrm{I}}|\Omega|g_{11}{}^{\mathrm{II}}\rangle\} + 2(-1)^{k-1}\{\langle f_1{}^{\mathrm{I}}|\Omega|g_7{}^{\mathrm{II}}\rangle - \langle f_1{}^{\mathrm{I}}|\Omega|g_8{}^{\mathrm{II}}\rangle + \langle f_1{}^{\mathrm{I}}|\Omega|g_{12}{}^{\mathrm{II}}\rangle\} + (-1)^{n-1}\{\langle f_1{}^{\mathrm{I}}|\Omega|g_9{}^{\mathrm{II}}\rangle + \langle f_1{}^{\mathrm{I}}|\Omega|g_{10}{}^{\mathrm{II}}\rangle - 2\langle f_1{}^{\mathrm{I}}|\Omega|g_{13}{}^{\mathrm{II}}\rangle + \langle f_1{}^{\mathrm{I}}|\Omega|g_{14}{}^{\mathrm{II}}\rangle\} \quad (4)$$

A discussion of the meaning of eq 3 and 4 is most easily done by assuming the bond functions to be calculated in a basis of orthogonal atomic orbitals with neglect of differential overlap. The contribution to the overlap integral $\langle\psi_{\mathrm{I}}|\psi_{\mathrm{II}}\rangle$ vanishes in this case; therefore we consider the Hamilton operator. Due to the neglect of overlap and differential overlap eq 3 and 4 reduce to

$$\Delta H_{\mathrm{I,II}}{}^{\mathrm{even}} = 2(-1)^{n-k}\{\langle f_1{}^{\mathrm{I}}|H|f_5{}^{\mathrm{II}}\rangle + \langle f_1{}^{\mathrm{I}}|H|f_6{}^{\mathrm{II}}\rangle\} + 2(-1)^{k-1}\{\langle f_1{}^{\mathrm{I}}|H|f_7{}^{\mathrm{II}}\rangle + \langle f_1{}^{\mathrm{I}}|H|f_8{}^{\mathrm{II}}\rangle\} \quad (5)$$

for two even-membered rings and to

$$\Delta H_{\mathrm{I,II}}{}^{\mathrm{odd}} = 2(-1)^{n-k}\{\langle f_1{}^{\mathrm{I}}|H|g_5{}^{\mathrm{II}}\rangle - \langle f_1{}^{\mathrm{I}}|H|g_6{}^{\mathrm{II}}\rangle\} + 2(-1)^{k-1}\{\langle f_1{}^{\mathrm{I}}|H|g_7{}^{\mathrm{II}}\rangle - \langle f_1{}^{\mathrm{I}}|H|g_8{}^{\mathrm{II}}\rangle\} \quad (6)$$

for two odd-membered rings.

As an example we consider the term $\langle f_1{}^{\mathrm{I}}|H|f_5{}^{\mathrm{II}}\rangle$. In the same way as before, it follows that this matrix element is determined by the ionic terms in the bond functions for the left ring and by the covalent terms for the right ring. The final result is

$$\langle f_1{}^{\mathrm{I}}|H|f_5{}^{\mathrm{II}}\rangle = 2^{-n}\left\{\prod_{i=1}^{2k-1}\mu_i\right\}\left\{\prod_{i=2k}^{2n}\nu_i\right\}\beta_{\mathrm{x}}$$

where β_{x} is the resonance integral for the non-nearest-neighbor interaction. For $\langle f_1{}^{\mathrm{I}}|H|f_6{}^{\mathrm{II}}\rangle$ we obtain the same result whereas for $\langle f_1{}^{\mathrm{I}}|H|f_7{}^{\mathrm{II}}\rangle$ and $\langle f_1{}^{\mathrm{I}}|H|f_8{}^{\mathrm{II}}\rangle$ μ and ν are interchanged. So, we obtain for two even-membered rings

$$\Delta H_{\mathrm{I,II}}{}^{\mathrm{even}} = 2^{-n+2}\left[(-1)^{n-k}\left\{\prod_{i=1}^{2k-1}\mu_i\right\}\left\{\prod_{i=2k}^{2n}\nu_i\right\} + (-1)^{k-1}\left\{\prod_{i=1}^{2k-1}\nu_i\right\}\left\{\prod_{i=2k}^{2n}\mu_i\right\}\right]\beta_{\mathrm{x}} \quad (7)$$

For two odd-membered rings it follows in the same way that

$$\langle f_1{}^{\mathrm{I}}|H|g_5{}^{\mathrm{II}}\rangle = \langle f_1{}^{\mathrm{I}}|H|g_6{}^{\mathrm{II}}\rangle$$

$$\langle f_1{}^{\mathrm{I}}|H|g_7{}^{\mathrm{II}}\rangle = \langle f_1{}^{\mathrm{I}}|H|g_8{}^{\mathrm{II}}\rangle$$

So,

$$\Delta H_{\mathrm{I,II}} = 0 \quad (8)$$

Equations 7 and 8 result in the aromaticity rules for polycyclic systems[2] which can be summarized as follows. The introduction of an extra bond in a $2n$-membered system does not change the resonance energy when the system is split into two odd-membered rings. In the case of two even-membered rings the resonance energy is enlarged when the separate rings are aromatic and diminished when the separate rings are not aromatic.

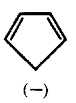
An interesting application of eq 7 and 8 is the forbidden or allowed character of the valence isomerizations of benzene. According to the Woodward–Hoffmann rules in the formulation given in ref 1, the interconversion of benzene and prismane should be thermally allowed and Woodward and Hoffmann need some further arguments to show why prismane is a stable molecule (ref 1, p 107). From eq 7, however, it follows that both the conversion to Dewar benzene and to prismane are forbidden because of the suprafacial formation of two four-membered rings.

The case of the benzvalene formation is much less simple. Haller[9] has published a correlation diagram for this reaction, but his diagram is in error because of an incorrect symmetry designation of the benzvalene π and π^* orbitals. In fact, the benzvalene formation is an example of a reaction for which correlation diagrams do not distinguish between suprafacial and antarafacial bond formations (ref 1, p 31). This is just the same conclusion as obtained from eq 8, because the new bonds in benzvalene form odd-membered rings and therefore do not change the resonance energy. So, the Woodward–Hoffmann rules as such do not apply to the benzvalene formation. From the unchanged resonance energy on introduction of the new bonds, we may, however, conclude that the activation energy will be less than in the case of the Dewar benzene and prismane formation and in this sense we may conclude that the benzvalene formation is "allowed."

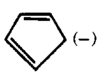
4. Odd-Membered Systems

4.1. Ionic Systems. The best known examples of aromatic odd-membered ring systems are the cyclopentadienyl anion and tropylium cation. Contrary to the preceding cases the aromaticity of these ionic species can be derived from the usual valence bond method[10] but here we will only consider the generalized approach introduced above.

Consider as an example the cyclopentadienyl anion. In this case there are five principal structures such as

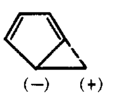


I

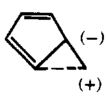


II

On neglect of non-nearest-neighbor interactions nonzero matrix elements are only obtained between structures with the charge on neighboring atoms. The Hamiltonian matrix element is then proportional to the β value between the atomic orbitals carrying the charge. The proportionality factor is most easily calculated by introduction of a positively charged "ghost orbital." The interacting structures with inclusion of the ghost orbital are



I



II

It follows immediately that the interaction between I and II can be treated in the same way as the non-nearest-neighbor interactions discussed in Section 3.

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(9) I. Haller, *J. Chem. Phys.*, 47, 1117 (1967).

(10) H. Fischer and J. N. Murrell, *Theor. Chem. Acta*, 1, 463 (1962–1963).

In the discussion in Section 2 and 3 the numbering of electrons in ψ_{II} was chosen in the same way as in the usual valence bond method. This facilitated a comparison with the Lu–O and Mu–O treatments. In the present case, however, it is somewhat easier to use instead of ψ_{II}

$$\Psi_{II}' = \{2^{N/2}/N!\}^{1/2} \sum_P{}' \epsilon_P P\alpha(1, 2)\beta(3, 4)\ldots\sigma(N,N + 1) \times [1, 2][3, 4]\ldots[N,N + 1]$$

which is different from ψ_{II} by a cyclic permutation of half the total number of electrons, and where N is now the number of carbon atoms in the ring. So, $\psi_{II}' = (-1)^{(N-1)/2}]\psi_{II}$. With this choice of wave function ψ_{II} is obtained from Ψ_I by a rotation over $360/N$ degrees. If all wave functions for the ring of N atoms are chosen in this way we have $H_{I,II} = H_{II,III} =$ etc. The symmetry of the ring is then introduced in a simple way. This is not possible with wave functions with an electron distribution corresponding to the usual valence bond method.

The total system including the ghost orbital now consists of two odd-membered rings. Therefore we must consider the functions $g_4', \ldots, g_{14}'$ corresponding to $g_4, \ldots, g_{14}$ used in eq 4. In the present case we have the additional condition that the ghost orbital should be positively charged. If we take the three-membered ring containing the ghost orbital to be the right ring, it follows that in the case of orthogonal atomic orbitals contributions are obtained from g_8 only. So, according to eq 6

$$\langle I|H|II\rangle_{neg} = 2(-1)^{(N-1)/2}\langle f_1^{I}|H|g_8^{II}\rangle$$

In the same way as before this yields

$$\langle I|H|II\rangle_{neg} = (-1)^{(N-1)/2}\left\{\prod_i \mu_i\right\}\beta/2^{(N-3)/2}$$

where i numbers the double bonds in structures I and II.

For positive ions it follows in the same way that we can only get contributions from g_7. This yields

$$\langle I|H|II\rangle_{pos} = -(-1)^{(N-1)/2}\left\{\prod_i \mu_i\right\}\beta/2^{(N-3)/2}$$

The secular problems obtained from all of the principal structures now become the same problems as in Heilbronner's molecular orbital discussion of normal and Möbius ring systems[11] but in the present case we must consider the lowest eigenstate only. The ionic odd-membered ring systems will be aromatic if this lowest eigenstate is nondegenerate. From the papers by Heilbronner[11] and by Zimmerman[3] it is easily inferred that the resulting aromaticity rule becomes: negatively charged normal ring systems and positively charged Möbius ring systems are aromatic if $(N - 1)/2$ is even whereas positively charged normal ring systems and negatively charged Möbius ring systems are aromatic if $(N - 1)/2$ is odd.

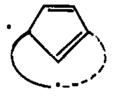
4.2. Neutral Systems. In the case of neutral odd-membered ring systems we introduce a ghost orbital containing one electron. Then the electron distribution is identical in all of the principal structures. This implies that nonzero matrix elements exist between all of these structures. We first consider the interaction between two structures with the unpaired electron on neighboring atoms.


I


II

The dots in these structures represent the fact that the bonds with the ghost orbital are purely covalent. Because of this covalency, the matrix element between I and II consists of terms corresponding to the first term of eq 1 and of terms corresponding to the contributions of g_5 and g_6 in eq 6. The latter contribution vanishes as in Section 3 whereas the first term of eq 1 does not differentiate between normal and Möbius ring systems.

As an example of the interaction between structures with the unpaired electron on nonneighboring atoms we consider



In this case the contributions corresponding to the nonneighboring interactions in eq 6 do not occur whereas the contributions corresponding to eq 1 are again independent of the normal or Möbius character of the ring. It thus follows that all of the matrix elements and consequently the energies of the ground states are identical for normal and Möbius ring systems. Neutral odd-membered rings can therefore be said to be nonaromatic as suggested before by Dewar.[2]

Appendix

Neglect of Non-Nearest-Neighbor Interactions. In Section 2 we have rederived the Mu–O result which states that in their particular approximation aromaticity depends on the product of all nearest-neighbor overlap integrals. In view of the orders of magnitude one might argue that it is inconsequent to consider such a term while simultaneously neglecting the non-nearest-neighbor interactions. We have not examined this problem in all details, but in this appendix we will show that in a large number of cases the non-nearest-neighbor interactions are not important in a discussion of aromaticity.

First of all, for the integrals $\langle f_1^{I}|f_1^{II}\rangle$, $\langle f_1^{I}|f_2^{II}\rangle$, and $\langle f_1^{I}|f_3^{II}\rangle$ discussed in Section 2 one can safely assume that non-nearest-neighbor interactions will not change the conclusions about sign. It then follows that we can only expect an influence on our results through permutations not considered above. These permutations are of different kind insofar as they may yield interaction terms depending on one, two, or more non-nearest-neighbor overlap integrals. We will only consider terms depending on one non-nearest-neighbor interaction.

From Section 3 it follows that interactions between two odd or even numbered atoms, *e.g.*, 1–3 interactions, do not influence the resonance energies because they split the total ring system into two odd membered rings (see eq 6 and 8). Odd–odd and even–even interactions can therefore be neglected.

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(11) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964).

The situation is more complex if one considers odd–even interactions, *e.g.*, 1–4 interactions.

Let us first consider the 1–4 interaction in an eight-membered ring. In this case the non-nearest-neighbor interaction splits the total system into a four- and a six-membered ring. If all overlap integrals are positive, it follows from eq 5 and 7 that the contributions to the resonance energy obtained from the two subsystems have opposite signs so the total contribution is small. If there is one negative overlap integral, terms occur in which both the four- and the six- membered rings are aromatic but these are compensated by terms in which both subsystems are nonaromatic. We thus may conclude that non-nearest-neighbor interactions have no influence on the aromatic or nonaromatic character of $4n$-membered rings ($n = 1, 2, 3, \ldots$).

Unfortunately, a similar conclusion cannot be made in the case of $(4n + 2)$-membered rings. *E.g.*, a 1–4 interaction splits a six-membered ring into two four-membered rings. Now, if all overlap integrals are positive as in benzene, both subsystems are nonaromatic so the 1–4 interaction diminishes the resonance energy. On the other hand, it must be noted that, just as in the case of 1–2 interactions, the 1–4 interactions enter the resonance energy through a product of all overlap integrals of the subsystem, so the difficulty is probably not too serious.

Acidity of Hydrocarbons. XLIV. Equilibrium Ion-Pair Acidities of 9-Alkylfluorenes in Cyclohexylamine[1]

A. Streitwieser, Jr.,* C. J. Chang, and D. M. E. Reuben

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received August 14, 1971*

Abstract: The pK values of several 9-alkylfluorenes were measured by the competition method with both cesium and lithium cyclohexylamides. The equilibrium constants of the Cs and Li salts are converted to pK values by taking the standard 9-phenylfluorene = 18.49 with both gegenions. The resulting pK values for Cs and Li, respectively, are: fluorene, 22.74, 22.50; methyl, 22.33, 22.60; ethyl, 22.60, 22.96; isopropyl, 23.20, 23.75; *tert*-butyl, 24.25, 24.82; benzyl, 21.27. The cesium acidities, except for *tert*-butyl but including benzyl, give a good $\rho\sigma^*$ correlation with $\rho = 4.55$. The relative acidities of 9-methylfluorene and fluorene are discussed. Temperature coefficients for most of the substituents were determined and the derived enthalpy and entropy values are discussed in terms of ion-pair interactions.

The relative acidities of conjugated hydrocarbons are important in structure–reactivity relationships. Different methods have been employed by different investigators[2] in various solvent systems in measurements of acidities of carbon acids. In our studies,[3] we have used a competition method of two hydrocarbons with insufficient strong base in cyclohexylamine to measure the equilibrium

$$R_1^-M^+ + R_2H \rightleftharpoons R_1H + R_2^-M^+ \quad (1)$$

The determination of the acidities of 9-alkylfluorenes is of considerable interest to help establish the nature of the electronic effect of alkyl groups at a sp^2-hybridized carbanion center. Bowden, Cockerill, and Gilbert,[4] using the H_- technique in dimethyl sulfoxide–water, reported the acidity of a series of 9-substituted fluorenes. One significant finding in their results is that 9-methylfluorene is more acidic than fluorene, contrary to the common expectation that alkyl groups are electron releasing and destabilize carbanions in solution. Ritchie and Uschold[5] also found 9-methylfluorene more acidic than fluorene in dimethyl sulfoxide. In both of these cases, the carbanions involved are free ions in a polar solvent. However, in cyclohexylamine, a relatively nonpolar solvent, the carbanions are present essentially entirely as ion pairs.[6]

Experimental Section

Materials Used. Fluorene (Fl), 2,3-benzfluorene (2,3-BF), and 9-methylfluorene were described previously.[7] 9-Benzylfluorene (9-BF) was prepared by treating fluorenyllithium with benzyl chloride, mp 134–135° (lit.[8] 135°). The rest of the 9-alkylfluorenes[9]

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[1] This research was supported in part by Grant No. 12855 of the National Institutes of Health, U. S. Public Health Service.

[2] For general reviews in this area, see: (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965; (b) A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, 3, 41 (1965); (c) H. Fischer and D. Rewicki, *Progr. Org. Chem.*, 7, 116 (1967); (d) H. F. Ebel, "Die Acidität der CH-Säuren," G. Thieme Verlag, Stuttgart, 1969.

[3] (a) A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *J. Amer. Chem. Soc.*, **89**, 59 (1967); (b) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *ibid.*, **89**, 63 (1967); (c) A. Streitwieser, Jr., C. J. Chang, W. Hollyhead, and J. R. Murdoch, *ibid.*, **94**, 5288 (1972).

[4] K. Bowden, A. F. Cockerill, and J. R. Gilbert, *J. Chem. Soc. B*, 179 (1970).

[5] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 1721 (1967).

[6] A. Streitwieser, Jr., W. M. Padgett, and I. Schwager, *J. Phys. Chem.*, **68**, 2922 (1964).

[7] A. Streitwieser, Jr., W. B. Hollyhead, A. H. Pudjaatmaka, P. H. Owens, T. L. Kruger, P. A. Rubenstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. M. Niemeyer, *J. Amer. Chem. Soc.*, **93**, 5088 (1971).

[8] G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **38**, 697, 2450 (1960).

[9] We thank Mr. S. Holten for preparing 9-methylfluorene, 9-ethylfluorene, and 9-*tert*-butylfluorene, Mr. R. MacQuarrie for preparing 9-isopropylfluorene, and Mr. J. Schafer for preparing 9-*tert*-butylfluorene.