Quantum Organic Photochemistry. II. Resonance and Aromaticity in the Lowest $^3\pi\pi^*$ State of Cyclic Hydrocarbons[1]

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Abstract: The concepts of aromaticity, antiaromaticity, and Dewar resonance energy are extended to the lowest $\pi\pi^*$ triplet state of conjugated hydrocarbons by comparing the bonding energy of triplets to the most stable biradical reference structure. Arguments based upon simple perturbation theory indicate that the rules for ground state aromaticity are reversed in the $^3\pi\pi^*$ state ($4n$ rings display "aromatic" character whereas $4n + 2$ systems display "antiaromaticity"). Semiempirical SCF–LCAO–MO calculations by the NNDO method confirm these predictions, and are used to predict transition, bonding, and stabilization energies for a wide range of triplets including those for cyclobutadiene and derivatives, cyclooctatetraene and derivatives, nonclassical polyenes, three- to seven-membered rings containing exocyclic carbon atoms, benzenoid hydrocarbons, butalene, azulene, and cyclodecapentaene. The preference of certain hydrocarbon triplets for a completely planar rather than 90° twisted structure (such as methylenecyclopropene, fulvene, and heptafulvene) is analyzed by perturbation theory. The consequences of aromatic and antiaromatic character to the exothermicity of ortho addition are explored for several hydrocarbon triplets.

The concepts of resonance energy and of aromaticity have proven invaluable in explaining and in predicting the structures, stabilities, and reactivities for the ground states of conjugated molecules. In this report, these concepts are extended to the lowest $\pi\pi^*$ *triplet state* of conjugated hydrocarbons by use of orbital correlation diagrams and simple one-electron perturbation theory. Predictions of the structure, stability, and reactivity for triplets based upon these models are compared with semiempirical SCF–LCAO–MO calculations for a variety of conjugated cyclic hydrocarbons.

Results and Discussion

Definition of Resonance Energy for Triplets. The aromaticity and resonance energy for a molecule are defined relative to its most stable valence-bond structure. Thus the resonance energy for the *ground state* of a cyclic, conjugated hydrocarbon such as benzene (**1a**) is judged relative to the energy "expected" for the most stable Kekulé structure (**1b**) which contains alternating double and single bonds. Perhaps the most useful definition of resonance energy for both thermochemical and theoretical purposes is that of Dewar, who proposed that the effective C=C and C–C bond energies used to calculate the energy of the reference structure should correspond to the effective energies for such bonds found in conjugated, acyclic polyenes.[2,3] The Dewar resonance energy (DRE) for an aromatic compound is significantly positive, for an antiaromatic system significantly negative, and close to zero for a (nonaromatic) ring system in which the structure and energetics are essentially those for an open-chain conjugated polyene.[2,3] In essence, the Dewar resonance energy (DRE) is a measure of the extra stabilization (or destabilization) associated with a ring system compared to the corresponding open-chain compound which contains the same number of conjugated carbon atoms. Note that the reference structure does not necessarily correspond to one with localized single and double bonds if the latter is not the most stable form for the chain;[2] for example, the DRE of the cyclopropenium cation **2** is judged relative to the bonding energy in the delocalized allyl cation **3a** rather than relative to the imaginary localized structure **3b**.

1a

1b

2

3a

3b

In this spirit, we propose that the *Dewar resonance energy* (and thus the aromaticity or antiaromaticity) *of the lowest $\pi\pi^*$ triplet state of a cyclic hydrocarbon be defined relative to the bonding energy for the lowest $^3\pi\pi^*$ state of the open-chain polyene which contains the same number of carbon atoms.* This definition is particularly easy to use since the most stable conformation for a polyene triplet has one internal C=C bond twisted 90°, and the energy for such a triplet is simply the bonding energies of the two corresponding free-radical chains joined by a "purely single" C(sp^2)–C(sp^2) bond.[1c,4] For example, the DRE and aromaticity of the cyclobutadiene triplet **4a** are judged by comparing its total calculated carbon–carbon bonding energy with that for an allyl free radical (with a CCC angle of 90°) plus the energy of two "purely single" C–C bonds (each 88.8 kcal mol^{-1}). In essence, then,

4a

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[1] (a) Publication No. 40 of the Photochemistry Unit. (b) Research supported by the National Research Council of Canada. (c) Part I: N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, **93**, 4427 (1971).

[2] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, Chapters 5 and 6.

[3] N. C. Baird, *J. Chem. Educ.*, **48**, 509 (1971).

[4] N. C. Baird, *Mol. Photochem.*, **2**, 53 (1970).

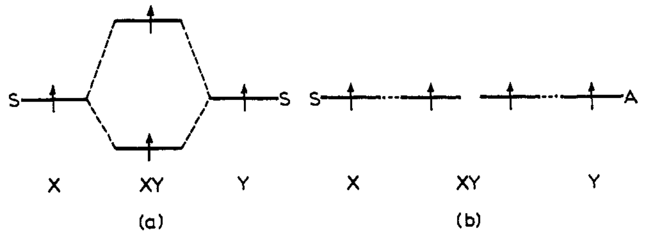


Figure 1. Type I interaction of NBMOs of radicals X and Y in triplet XY for (a) $4n + 2$ rings and (b) $4n$ rings.

the resonance (or stabilization) energy of a cyclic triplet is its calculated bonding energy less that for the pair of odd-electron conjugated radical chains which, when linked by σ bonds, yields the most stable reference structure.[5]

Orbital Interactions in Triplets. The sign and magnitude of the Dewar resonance energy (and thus the aromaticity or antiaromaticity) for planar, cyclic hydrocarbon triplets are dependent upon the manner in which the molecular orbitals of one free-radical unit in the reference structure interact with the MOs of the other. In this section, such orbital interactions are analyzed by a combination of the correlation diagram technique popularized by Woodward and Hoffmann[6] and the one-electron perturbation MO scheme developed by Dewar.[2] The analysis below considers only the interactions which *dominate* the total energy change; *i.e., the influence of conjugation between the singly-occupied MO of one radical unit X (or Y) with all the MOs of the other radical Y (or X), and vice versa.*[7]

Using the conventions adopted previously, the MOs of X and Y are symbolized ϕ_X and ϕ_Y, whereas the MOs for the triplet XY which results when X and Y interact across bonds r–s, r′–s′, etc., are symbolized ψ_{XY}. *The interactions between the singly-occupied MO of X with the singly-occupied MO of Y is termed the type I effect, whereas interactions between the singly-occupied MO of X (or Y) with the vacant and doubly-occupied MOs of Y (or X) are termed type II effects.*

Type I Effects. The interaction between the singly-occupied MO, ϕ_X, of X with that, ϕ_Y, of Y yields two new MOs, ψ^{+}_{XY} and ψ^{-}_{XY}, both of which are singly occupied in the lowest triplet state of XY. As shown previously,[1c] *any stabilization of* ψ^{+}_{XY} *relative to the average energy* ϵ_0 *of* ϕ_X *and* ϕ_Y *is more than offset by a greater destabilization of* ψ^{-}_{XY}. Thus the *total* change ΔE^{I} due to this type I interaction is always zero or destabilizing: $\Delta E^{\mathrm{I}} \leqslant 0$.

Extension of eq 9 in ref 1c to deal with multiple linkages between two radicals yields

$$\Delta E^{\mathrm{I}} = \frac{2S[\beta - \epsilon_0 S]\left(\sum_{\mathrm{r,s}} C_{\mathrm{Xr}} C_{\mathrm{Ys}}\right)^2}{1 - S^2\left(\sum_{\mathrm{r,s}} C_{\mathrm{Xr}} C_{\mathrm{Ys}}\right)^2}$$

where β and S are the standard resonance and overlap integrals between a pair of atomic orbitals χ_r and χ_s newly linked in the triplet, the terms C_{Xr}, etc., represent the expansion coefficients of the AOs in the isolated radical orbitals

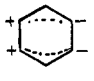
$$\phi_X = \sum_{\mathrm{r}}^{(\mathrm{X})} C_{\mathrm{Xr}} \chi_{\mathrm{r}}$$

$$\phi_Y = \sum_{\mathrm{s}}^{(\mathrm{Y})} C_{\mathrm{Ys}} \chi_{\mathrm{s}}$$

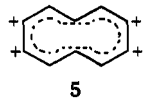
and the summation $\Sigma_{\mathrm{r,s}}$ runs over all bonds which link the two radical fragments in the triplet (*i.e.*, the "new" bonds). Since the singly-occupied MOs are either nonbonded molecular orbitals (NBMOs) for which $\epsilon_X = \epsilon_Y = \alpha$, or have energies close to α, then $\beta > \epsilon_0 S$ from which one deduces that $\Delta E^{\mathrm{I}} < 0$ if $\Sigma_{\mathrm{r,s}} C_{\mathrm{Xr}} C_{\mathrm{Ys}} \neq 0$ and $\Delta E^{\mathrm{I}} = 0$ if $\Sigma_{\mathrm{r,s}} C_{\mathrm{Xr}} C_{\mathrm{Ys}} = 0$.

In many cases, the systems X, Y, and XY all have a symmetry plane perpendicular to the plane of the molecule; the singly-occupied MOs then are either symmetric (S) or antisymmetric (A) with respect to reflection in this plane. In general $\Delta E^{\mathrm{I}} < 0$ if ϕ_X, ϕ_Y are both of the same symmetry (*i.e.*, AA or SS), and $\Delta E^{\mathrm{I}} = 0$ if ϕ_X, ϕ_Y are of different symmetry (*i.e.*, AS or SA). Now for unbranched free-radical chains, the NBMO wave functions[8] are of (i) S symmetry for chains with $4k + 1$ carbons (1, 5, 9 . . .) and (ii) A symmetry for chains with $4k + 3$ carbons (3, 7, 11 . . .). Two connected chains with S symmetry then yield a ring system with $4n + 2$ carbon atoms ($n = k_X + k_Y$) as do two chains of A symmetry ($n = k_X + k_Y + 1$); thus *triplets containing a periphery of 4n + 2 carbon atoms are subject to a type I destabilization.* In contrast, two connected chains of opposite symmetry yield a ring with $4n$ carbon atoms ($n = k_X + k_Y + 1$); thus *triplets containing a periphery of 4n carbon atoms have a zero type I interaction energy.*

The energy level splitting diagrams due to type I interactions for the $4n + 2$ and $4n$ carbon rings are illustrated in Figures 1a and 1b, respectively. In the molecular diagrams below, the + and − signs indicate the NBMO amplitudes for the $p\pi$ orbitals (upper lobes) for several $4n + 2$ systems (benzene (**1c**), cyclodecapentaene (**5**), and naphthalene (**6**)) and for two $4n$ systems (cyclobutadiene (**4b**) and cyclooctatetraene (**7**)). Note that in the $4n + 2$ systems, the coefficient *products* C_rC_s across both the bonds joining the radicals have the same sign, so the sum must be nonzero. In contrast, the product C_rC_s at one link of a $4n$ system

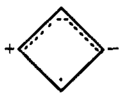


1c

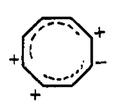


5

6



4b



7a

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[5] Purely single C–C bond energies[1c] are used in the reference structure rather than the energy for polyene C–C ground state structures since one bond is twisted (and thus is "purely single") in the most stable form of the polyene triplet.

[6] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

[7] The interactions *neglected* in the simple analysis correspond to those between doubly-occupied MOs of X with vacant MOs of Y and vice versa. The *overall* effect on the energy from such interactions is small or zero for small rings, and is usually stabilizing by a few kcal mol^{-1} in larger systems. Of course *all* interactions are included in the SCF calculations discussed in the next section.

[8] See for example Chapters 2 and 7 of ref 6.

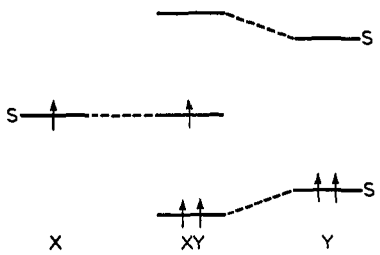

Figure 2. Type II interaction of NBMO of X with conjugate MO pair of Y in triplet XY. Both X and Y are assumed to be odd alternant systems.

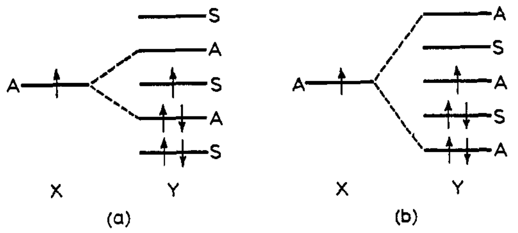

Figure 3. Type II interaction in (a) $4n$ ring triplets and (b) $4n + 2$ ring triplets.

has magnitude equal and opposite to that at the second link, so the products must add to zero. For systems without useful planes of symmetry, the value of the type I interaction can be deduced readily from knowledge of the signs and magnitudes for the NBMO coefficients which are easily computed by hand for odd alternant radicals.[1c,2]

Type II Effects. Primary type II effects are defined as the overall energy change due to the interaction of the singly-occupied MO of radical X with that *conjugated pair* of MOs (one doubly-occupied and bonding, the other vacant and antibonding) of radical Y which lie closest in energy to ϕ_X, and vice versa. The effects of the interaction are illustrated in Figure 2 for the case of two alternant radicals; the doubly-occupied MO is stabilized by the interaction, the vacant MO is destabilized, but the level associated with the singly-occupied MO is unaltered in energy. The net effect on the overall energy is always stabilizing, except when no appropriate pair of conjugated MOs of the correct symmetry is available; *i.e.*, $\Delta E^{II} \geqslant 0$. Unlike the type I effect, this conclusion applies whether or not overlap integrals are included in the calculations. From the analysis in the Appendix, the magnitude of ΔE^{II} is given by

$$\Delta E^{II} \sim 2\beta[(d^2 + 2k)^{1/2} - d]$$

if both radicals are odd-alternant systems. Here d is a measure of the energy gap between the singly-occupied MO ϕ_X of one radical and the doubly-occupied MO ϕ_Y of the other with which it interacts, and $k = \Sigma C_{Xr}C_{Ys}$. *Thus the interaction is greater the smaller the energy gap d and the larger the coefficient product k across all bonds newly created in the triplet.*

In general, the primary type II stabilization is larger for a system in which the type I interaction is zero (*e.g.*, $4n$ annulene triplets) than for systems which undergo a type I destabilization (*e.g.*, $4n + 2$ ring triplets) as a consequence of symmetry pattern for MOs in odd alternant radicals (*i.e.*, S, A, S, A, S...). If the type I interaction is zero, the singly-occupied MOs must be of opposite symmetry, with the result that the highest doubly-occupied MO of Y (or X) and the lowest vacant MO of Y (or X) must be of the same symmetry as the singly-occupied MO of X (or Y) (see Figure 3a). Thus the energy gap d is small in this case, and the net interaction must be significantly stabilizing. In contrast, if the type I interaction is nonzero, then the two singly-occupied MOs are of identical symmetry; thus the primary type II interaction must occur between the singly-occupied MO of X (or Y) with the *second-highest* doubly-occupied and the *second-lowest* vacant MOs of Y (or X) (see Figure 2b).[9] Since the energy gap now is relatively large, the type II stabilization is smaller than in the previous case. In the extreme case of benzene, the net type II effect is exactly zero since there are no appropriate bonding or antibonding orbitals of A symmetry on the allylic radical fragments.

Since the type I effect of interaction is always destabilizing for a $4n + 2$ ring triplet, and since the type II stabilization may not be large enough to compensate for this energy loss, it is conceivable that some $4n + 2$ ring triplets are antiaromatic in the sense that the total bonding energy is less stable than the energy sum for the two free-radical chains in the reference structure plus the appropriate number of purely single C–C bonds. In addition to their low stability, $4n + 2$ ring triplets should also display rather low symmetry in order that the two radical subunits interact as little as possible.[10]

In contrast, for $4n$ carbon rings the type II stabilization is always substantial and the type I effect is always zero; thus *the lowest triplet state for 4n rings is aromatic* since the bonding energy is significantly greater than for the diradical reference structure. Such molecules should exhibit the highest possible degree of symmetry in the triplet, since contraction of the single bonds connecting the radical subunits increases the (favorable) energy of interaction.

Thus the rules for aromaticity and antiaromaticity are exactly *reversed* in the lowest $^3\pi\pi^*$ state of annulenes; the $4n$ rings are aromatic and the $4n + 2$ rings antiaromatic in such triplets. The consequences of this behavior on the energetics, structure, and reactivity of annulene and other hydrocarbon triplets are discussed for individual cases in the next section.

"Aromatic" Triplets. The predictions based upon simple perturbation theory that $4n$ carbon rings should display aromatic character in the lowest triplet state have been tested by SCF–LCAO–MO calculations by the NNDO method,[1c,11] a theory in which *all* interactions between electrons in π-molecular orbitals (including electron–electron repulsions) are considered explicitly, and in which σ-bond energy effects are included "empirically" by use of the calculated SCF triplet bond

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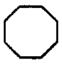
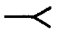
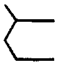
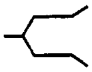
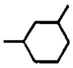
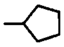
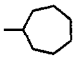
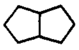
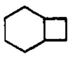
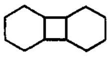
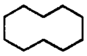
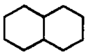
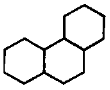
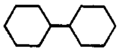
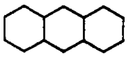
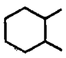
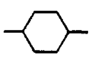
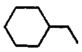
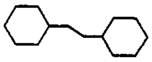
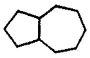
(9) Of course type II interactions can occur between the singly-occupied MO of X (or Y) with other conjugate sets of MOs of Y of the correct symmetry (if any). The effects of these ("nonprimary") additional interactions should be smaller in annulenes, however, than the "primary" interaction considered above since the energy gaps d will be larger and the coefficient products smaller (in general the more bonding a radical MO, the smaller the coefficients at the chain ends).

(10) This parallels the behavior of ground state antiaromatic systems such as cyclobutadiene in which the "alternating" rectangular structure of D_{2h} symmetry is more stable than the square D_{4h} conformation.[2,3]

(11) (a) N. C. Baird, *Mol. Phys.*, **18**, 29 (1970); (b) *Can. J. Chem.*, **49**, 338 (1971).

Table I. Energetics (kcal mol^{-1}) for Lowest ${}^3\pi\pi^*$ Triplet States of Hydrocarbons

No.	Hydrocarbon structure	Bonding energy[a,b]	Stabilizn energy[a] rel to Most stable chain pair[c]	Ref struct in text[d]	Rotation barrier[e]	$S_0 - T_1$ transition energy Calcd[f]	Exptl[g]
		Part A. "Aromatic Systems"					
4		435.5	+14.1	+14.1		20.8	
7		917.3	+17.7	+17.7		27.4	
8		340.2	+9.8	+9.8	+9.8		
9		579.8	+7.8	+7.8	+9.8		
10		817.8	+6.5	+6.5	+7.8		
11		918.3	+17.7	+6.8	+6.7		
12		406.1	−12.1	+8.2	+8.2	60.4	
13		676.8	+14.5	+3.9	+3.9	37.6	
14		906.7	+7.2	+7.7	+7.7	40.9	
15		1018.5	+27.1	+14.4		24.3	
16		494.7	−15.5	−8.0		39.7	
17		1009.7	+16.2	+9.0		38.9	
18		1585.8	+25.7	+13.0		51.9	
19		761.9	+7.9	+13.8		34.8	
		Part B. "Antiaromatic Systems"					
1c		644.4	−16.4	−16.4			
1d		648.5	−12.3	−12.3		83.4	84.4
5		1141.4	−0.8	−0.8		49.6	
6		1240.4	+7.4	−1.5		67.7	60.8
20		1819.0	+22.9	−4.0		69.2	62.1
21		1479.5	+10.8[h]	−4.1		74.7	65.0
22		1827.8	+31.4	+4.8		52.3	42.7
23		910.4	+9.8	−1.1	−1.1		
24		911.4	+13.9	−0.1	−0.1		
25		901.1	−1.4	−10.4	−10.4	67.9	50–62[j]
26		1730.9	+25.7	−3.3	−3.3	60.6	42–51[j]
27		1247.4	+13.3	+3.9		38.0	

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[a] Bonding and stabilization energies refer to the most stable *planar* structure. No σ-bond strain energy effects are included. [b] Bonding energy does not include the energy associated with the C–H bonds (each 97.7 kcal mol^{-1}, see ref 1c). [c] "Chain pair" reference structure is the total energy for the most stable pair of free radical chains (with same bond angles and dihedral angles as in triplet) plus the energy for that number of C–C single bonds required to unite the radicals. Thus the stabilization energies in this column are Dewar resonance energies. [d] Relative to energy for a reference structure containing two radicals joined by two σ bonds (one bond for systems with one or two exocyclic carbons) such that the maximum number of rings found in the triplet are present in the reference structure. In most cases, the reference structure is defined in the text. [e] Corresponds to energy difference between the 0 and 90° twisted conformation about the bond indicated by dashes in the figures, unless indicated otherwise. A negative barrier indicates the twisted form is energetically more stable than the planar. [f] Calculated $S_0 - T_1$ values refer to the *planar* molecules. For styrene and *trans*-stilbene, the real $S_0 - T_1$ energy should correspond to this value *less* the calculated barrier and an effect due to relief of steric strain. For cyclooctatetraene, see ref 13. [g] From ref 18. [h] For **21**, the reference structure is two cyclopentadienyl radicals plus an ethylene unit joined by four σ bonds. [i] For **26**, the reference structure is two cyclopentadienyl radicals plus a *trans*-butadiene unit joined by four σ bonds. [j] See the discussion in ref 4.

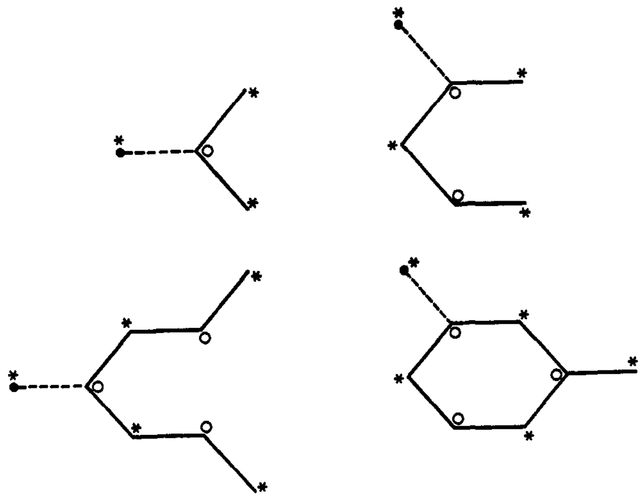


Figure 4. Type I interaction of NBMOs in triplet state for nonclassical hydrocarbons. The asterisks represent carbons "active" in the NBMOs, the zeros represent "inactive" carbon atoms.

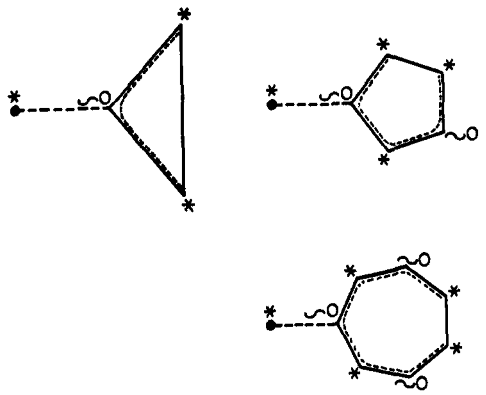
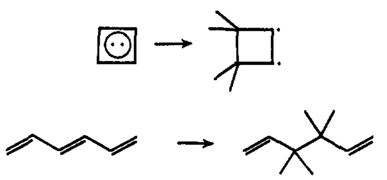


Figure 5. Type I interactions of singly-occupied MOs in triplet states of methylenecyclopropene, fulvene, and heptafulvene.

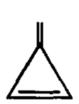
distances and Morse functions.[12] The calculated bonding and stabilization energies for all "aromatic" triplets are listed in Table I, part A.

The net stabilization energies calculated for the cyclobutadiene (**4**) and cyclooctatetraene (**7**) triplets relative to their component radicals (allyl plus methyl, and pentadienyl plus methyl, respectively) plus twice E_{C-C} are quite large at 14.1 and 17.7 kcal mol^{-1}, respectively. As expected, all bond lengths are equal in the optimum geometries for both cases (1.43 Å for **4**, 1.41 Å for **7**). Since the ground states of both are antiaromatic and their triplet states both aromatic, the calculated S_0-T_1 transition energies calculated for both cyclobutadiene and cyclooctatetraene of 21 and 27 kcal mol^{-1}, respectively,[13] are much smaller than for their open-chain polyene analogs butadiene and octatetraene (53 and 40 kcal mol^{-1}, respectively). The aromaticities of the triplet states of both **4** and **7** are also evident from the viewpoint of reactivity; for example, the energy gain obtained by ortho addition is calculated to be 35 and 21 kcal mol^{-1} less than for the same process for an inner C=C bond in the ground state of a polyene chain. (By contrast, the ortho localization energy for the benzene ground state is 21 kcal mol^{-1} less than the polyene value.)

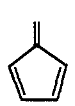


The extension of the simple perturbation theory arguments to chains and to rings with exocyclic carbon atoms leads to several interesting predictions which can be tested by NNDO calculations. For example, the type I interaction should be zero and the type II interaction should be stabilizing for triplets formed by union of a methyl radical to an "inactive" carbon in a conjugated radical chain (*i.e.*, to an atom the NBMO coefficient for which is zero, as indicated by a zero rather than by an asterisk in the diagrams to follow). Since such union always results in the formation of a nonclassical polyene (*i.e.*, one for which a complete set of alternating double and single bonds cannot be written for the ground state), the simple theory predicts that *a completely planar structure is preferred as the equilibrium conformation for nonclassical polyene triplets* (in contrast to classical polyenes which prefer one bond twisted by 90° in the triplet state). This prediction is confirmed by NNDO calculations for trimethylenemethane (**8**), 2-methylenepentadienyl (**9**), and 4-methyleneseptatrienyl (**10**); the calculated barriers to rotation about the "new" bonds (see Figure 4) are 9.8, 9.7, and 7.8 kcal mol^{-1}, respectively. Thus the conformational stability of such triplets to bond rotation should be of the same order of magnitude as in the allyl free radical.

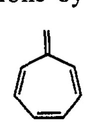
The arguments given above can be extended immediately to nonclassical ring compounds formed by union of methyl with an alternant radical. Thus the lowest triplet state of *m*-xylylene (**11**) resists exocyclic 90° bond rotation by 6.7 kcal mol^{-1}, since it is formed by union of methyl to an inactive carbon of the benzyl radical (see Figure 4). Although free-radical rings containing a periphery with an *odd* number of carbon atoms are nonalternant systems, the coefficients in the singly-occupied MO are close to those for the corresponding acrylic system in the equilibrium conformation of the molecule (*i.e.*, a "long" bond joining the ends of the chain radical[14]). The coefficients at ring positions which are "inactive" in the chain are *close* to zero for such rings, with the result that the type I destabilization should be small, and the type II stabilization significant, when an exocyclic carbon is bonded to the quasi-inactive positions (Figure 5). In accord with this analysis, the NNDO calculations predict that the planar triplet states of methylenecyclopropene (**12**), of fulvene (**13**), and of heptafulvene (**14**) are more stable than the 90° twisted conformations by 8.2, 3.9,



12



13



14

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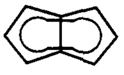
[12] All calculated values quoted in this and the following section have been calculated using the NNDO method. No configuration interaction has been included except where indicated otherwise. Open-shell calculations were executed using the "half-electron" procedure (see ref 1c).

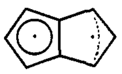
[13] The actual 0-0 band for 7 should be larger than this value since the equilibrium conformation of the ground state is taken as planar in the calculations.

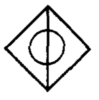
[14] N. C. Baird, unpublished calculations.

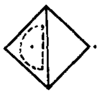
and 7.7 kcal mol^{-1}, respectively. Thus isomerization about the exocyclic C=C bond in **12**, **13**, and **14** should be relatively slow when sensitizers of energy close to the 0–0 band of the $S_0 - T_1$ transition (see Table I) are employed, in direct contrast to the open-chain polyene analogs of the systems for which 90° twisting is an exothermic process.[1c]

Polycyclic rings containing 4*n* carbon atoms (all located on the periphery) also display aromatic character in their lowest triplet states. For such systems, however, the total resonance energy (Dewar resonance energy) computed relative to the most stable pair of radical chains is not as informative with respect to the type I and II interactions as is the stabilization relative to the most stable radical pair with the same network of bonds. For example, the Dewar resonance energy predicted by NNDO for the pentalene triplet **15a** is 27.1 kcal mol^{-1}, which is significantly greater than that for **7** itself.[15] Relative to a cyclopentadienyl radical linked by two single bonds to an allyl radical (**15b**), however, the stabilization energy is only 14.4 kcal mol^{-1}. Similary, the apparent negative Dewar resonance energy for the bicyclobutadiene triplet **16a** is due to the significant antiaromaticity of the component cyclopropenyl ring; relative to the three-membered ring plus a methyl radical (**16b**) the interaction is +8.0 kcal mol^{-1}.

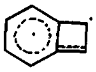

15a


15b

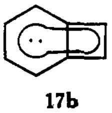

16a

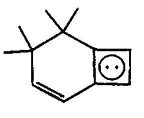

16b

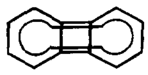
The lowest triplet states of benzcyclobutadiene (**17**) and of biphenylene (**18**) are predicted also to be more stable than their benzylmethyl and benzylpentadienyl reference structures (**17a** and **18a**) by 9.0 and 13.0 kcal mol^{-1}, repectively. Although the bond lengths predicted for **17** indicate an optimum structure (**17b**) equivalent to cyclooctatetraene linked 1,4 by a long single bond, the ortho localization energy (to yield **17c**) is only 9 kcal mol^{-1} less exothermic than for a polyene, since the product (**17c**) contains a four-membered ring in the triplet, the aromaticity for which is only slightly less than for an eight-membered ring. Similarly, the calculated structure for the biphenylene triplet (**18b**) is a simulation of a 12-carbon ring linked by two single bonds; α,β addition within the benzene ring requires only 9 kcal mol^{-1} more energy than for a polyene ground state, since the resulting product retains the benzcyclobutadiene aromaticity.


17a


18a


17b

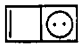

17c


18b

Although the resonance energies for the triplet states of **6**, **17**, and **18** are not dissimilar, the antiaromaticity of the ground states decreases substantially as benzene rings are fused to cyclobutadiene, with the result that the $S_0 - T_1$ energies *increase* in the order given in Table I. In connection with low $S_0 - T_1$ transition energies associated with systems containing four-membered rings, the butalene molecule (**19**) should also be mentioned. Although its periphery contains $4n + 2$ carbon atoms, the calculated triplet energy yields an aromaticity of +7.9 kcal mol^{-1}, since the system is really a resonance hybrid of the two cyclobutadiene–ethylene systems **19b** and **19c**. Since the triplet is aromatic and the ground state slightly antiaromatic, the predicted $S_0 - T_1$ energy is relatively low at 34.8 kcal mol^{-1}.

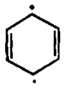

19a


↔


19b **19c**

Antiaromatic Triplets. The prime example of triplet state antiaromaticity occurs in the diallylic form of benzene, for which the type I destabilization is large and the type II stabilization is zero. The NNDO calculations predict that the optimum planar diallylic structure **1c** is 16.4 kcal mol^{-1} less stable than two allylic radicals joined by two single bonds, and that the two single bonds are slightly longer (1.51 Å) than the NNDO value for a "purely single" C(sp^2)–C(sp^2) bond (1.496 Å). Since the antiaromaticity of the diallylic form is approximately equal and opposite to the delocalization energy for two allyl radicals, it is not surprising that the "biquinoidal" form **1d** (in which the allylic stabilization and the type I destabilization both vanish) is essentially isoenergetic with **1c**; in fact, the optimum planar form for **1d** (calculated bond lengths of 1.36 and 1.47 Å) is predicted by NNDO to be 4.1 kcal mol^{-1} more stable than the planar form of **1c**. Although the introduction of extensive configuration interaction into the calculations reduces this difference to 1.7 kcal mol^{-1}, the essential prediction that the D_{2h} forms of triplet benzene are substantially more stable than the D_{6h} structure (by ~15 kcal mol^{-1} according to NNDO–CI calculations) remains unchanged.[16] Recent experimental information from several sources confirms the loss of D_{6h} symmetry in the lowest benzene triplet[17] and even suggests a nonplanar structure; un-


1c


1d

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(15) See also N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, **93**, 3072 (1971).

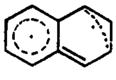
(16) The prediction that the 1c and 1d forms of triplet benzene are more stable than the D_{6h} structure was made originally by J. H. van der Waals, A. M. D. Berghuis, and M. S. de Groot, *Mol. Phys.*, 13, 301 (1967).

(17) (a) D. M. Burland, G. Castro, and G. W. Robinson, *J. Chem. Phys.*, **52**, 4100 (1970); (b) A. M. P. Goncalves and C. A. Hutchinson, Jr., *ibid.*, **49**, 4235 (1968).

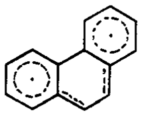
fortunately energetic calculations for nonplanar rings involve estimations of σ-bond strain energy effects, factors which cannot be handled by the NNDO π-electron method.

The resonance energies and $S_0 - T_1$ transition energies (0–0 band) for several benzenoid hydrocarbons are listed in Table I, part B. With the exception of benzene, the calculated $S_0 - T_1$ energies are too high by 7–10 kcal mol^{-1} compared with the experimental;[18] zero-differential overlap calculations by Dewar and Trinajstic[19] for the same hydrocarbons gave errors of similar magnitude but opposite sign. In the case of the NNDO calculations, the error for these systems is probably due to an inherent underestimation of the stability of the benzyl radical itself.[14]

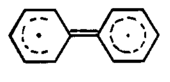
Although both the naphthalene (**6**) and phenanthrene (**20**) triplets are predicted to be substantially more stable (*i.e.*, possess positive Dewar resonance energy) than the corresponding radical chains linked by three single bonds, some residual type I destabilization is evident when the most stable reference structures are used for comparison. Thus naphthalene is calculated to be 1.5 kcal mol^{-1} *less* stable than a benzylallyl radical pair linked by two single bonds (**6a**), phenanthrene is 4.0 kcal mol^{-1} less stable than two benzyl radicals joined by two bonds (**20a**), and biphenyl (**21**) is 1.7 kcal mol^{-1} less stable than the benzylpentadienyl reference structure (**21a**). Evidently the type II stabilization outweighs the type I destabilization in anthracene (**22**), since its triplet is 4.8 kcal mol^{-1} more stable than the dibenzyl reference structure (**22a**).



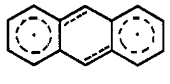
6a



20a



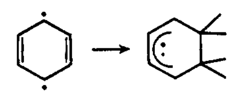
21a

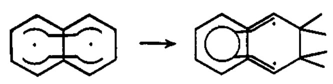


22a

The $S_0 - T_1$ transition energy for phenanthrene is correctly predicted to be much greater than for anthracene (and even larger than for naphthalene, also in agreement with experiment); the greater ground state aromaticity and greater triplet state aromaticity for phenanthrene compared with anthracene are *together* responsible for the large difference in $S_0 - T_1$ energies between the two isomers. The calculated bond distances for **6**, **20**, **21**, and **22** triplets agree well (within ±0.01 Å) with those calculated by Dewar and Trinajstic,[19b] with the exception of the length of the 9,10 bond in phenanthrene. The NNDO value of 1.46 Å for this link is significantly longer than the value (1.42 Å) predicted by Dewar and Trinajstic, presumably because the zero-differential overlap calculations ignore type I destabilization which in phenanthrene occurs primarily across the 9,10 bond.

The antiaromaticity associated with the triplet state of benzenoid hydrocarbons is predicted to yield drastic changes in the intermolecular reactivity compared to the ground state. For example, ortho localization in the benzene triplet is predicted to be 4 kcal mol^{-1} more exothermic than for a polyene ground state, compared to the 21 kcal mol^{-1} decrease in exothermicity predicted for the benzene ground state. For naphthalene, anthracene, and phenanthrene, the most stable products resulting from ortho localization reactions are all "nonclassical" orthobiquinoidal triplets; the reaction exothermicities are only 3, 11, and 10 kcal mol^{-1} less than for a polyene ground state. In this context it is interesting to note that both the ortho (**23**) and para (**24**) isomers of xylene suffer from type I destabilization in the triplet (Figure 6), in contrast to the meta isomer (**11**). The NNDO calculations for **23** and **24** predict that the conformations in which one exocyclic bond is twisted 90° are 1.1 and 0.1 kcal mol^{-1}, respectively, more stable than the completely planar forms. The type I destabilization is larger still in styrene (**25**) and in *trans*-stilbene (**26**); here the conformations twisted 90° about the exocyclic C=C bond are predicted to be 10.4 and 3.3 kcal mol^{-1} more stable than the planar. It is interesting that the NNDO calculations predict a barrier of ~5 kcal mol^{-1} (peak at ~45°) which must be overcome in **26** before the more stable 90° twisted conformation is achieved.[20]





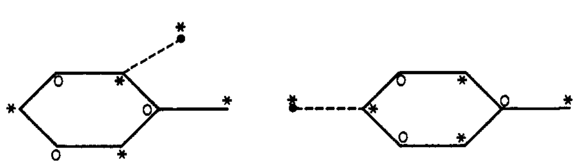
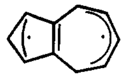


Figure 6. Type I interactions in *o*- and *p*-xylenes.

Finally, NNDO calculations have been performed for two 10π-electron nonbenzenoid ring systems containing fused rings azulene (**27**) and cyclodecapentaene itself (**5**). The total triplet Dewar resonance energy for azulene is larger than for naphthalene (in contrast to the ground state), since the former contains an "aromatic" cyclopentadienyl radical subunit; the total type I destabilization is reduced by the adoption of bond lengths which simulate two noninteracting radicals plus a double bond (**27a**). The net Dewar resonance energy for cyclodecapentaene of −0.8 kcal mol^{-1} indicates that the type II stabilization almost overcomes the type I destabilization for this member of the $4n + 2$ annulene series. Thus the antiaromaticity of the $4n + 2$ triplets diminishes as quickly with in-



27a

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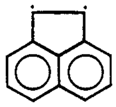
(18) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, Chapter 3.

(19) (a) M. J. S. Dewar and N. Trinajstic, *Chem. Commun.*, 646 (1970); (b) *J. Chem. Soc. A*, 1220 (1971).

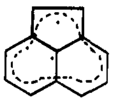
(20) Small intermediate barriers are also predicted for C=C bonds in some polyenes[1c] and in other rings with exocyclic carbons.

creasing ring size as does the antiaromaticity of 4*n* ring systems in the ground state.[2,8]

In a future publication, the present calculations will be extended to larger nonalternant hydrocarbons such as calicene systems and fused ring systems with multiply-connected π-electron pathways. The aromaticity analysis is more complex in many such cases, however, since the $\pi\pi^*$ excitation tends to be "localized" within a subunit of the molecule. For example, the lowest triplet of acenaphthylene (**28**) has a larger contribution from **28a** (excitation localized at an ethylenic bond) than from structures such as **28b** in which the excitation is delocalized across the entire π network.



28a



28b

Appendix

Assuming zero overlap, the energies for two conjugate MOs are $\alpha + y\beta$ and $\alpha - y\beta$ for alternant radicals. If the radical ends are joined, then by the pairing theorem, the interaction matrix elements between both the bonding and the antibonding MO with an NBMO on the second alternant radical have identical magnitude, say $k\beta$. Thus the secular determent to be solved for the three-orbital interaction is then

$$\begin{vmatrix} \alpha + y\beta - \epsilon & 0 & k\beta \\ 0 & \alpha - y\beta - \epsilon & k\beta \\ k\beta & k\beta & \alpha - \epsilon \end{vmatrix} = 0$$

The three roots are $\epsilon_1 = \alpha + \beta(y^2 + 2k)^{1/2}$, $\epsilon_2 = \alpha$, and $\epsilon_3 = \alpha - \beta(y^2 + 2k)^{1/2}$. Since ϵ_1 is occupied by two electrons and ϵ_2 by one, the net stabilization energy is

$$\Delta E^{\text{II}} = 2\epsilon_1 - 2(\alpha + y\beta) + \epsilon_2 - (\alpha)$$
$$= 2\beta[(y^2 + 2k)^{1/2} - y]$$

Hydrogen Bonding of Phenol with Acetylenes and Allenes[1]

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Contribution from the Department of Synthetic Chemistry,
Kyoto University, Yoshida, Kyoto 606, Japan. *Received July 31, 1971*

Abstract: Hydrogen bonding between phenol and acetylene or allene derivatives was studied by measuring the hydroxyl stretching absorption band. The frequency shifts and the thermodynamic values were evaluated. The basicity of acetylenes is larger than that of allenes and olefins, which are of the same order of magnitude. The equilibrium constants and the entropy changes in the formation of complexes with acetylenes are much larger than those with olefins and allenes. Two bonded OH bands are noted with arylacetylenes, but not with aliphatic acetylenes and allenes. Arylacetylenes act as bifunctional bases toward phenol, while allenes seem to act as monofunctional bases.

It is well known that unsaturated organic compounds act as proton acceptors for hydrogen bonds.[2] Although a number of investigations have been directed toward the intermolecular hydrogen bond with aromatic hydrocarbons,[3-5] relatively little work has been done on the intermolecular hydrogen bond with olefins,[6] allenes, and acetylenes.[7-9] The authors of these papers reported only the frequency shifts of ν_{OH} due to hydrogen bond formation.

As allenes can undergo two types of double bond isomerizations, that is either acetylene and/or conjugated diene formation,[10,11] the study of hydrogen bonding with acetylenes and allenes might give useful information on their properties as carbon bases. This paper includes the frequency shifts ($\Delta\nu$) of ν_{OH} of phenol and the thermodynamic values in the hydrogen-bonded complex with acetylenes and allenes. From these results the characteristics of the complexes involving the acetylene and allene derivatives are discussed in comparison with those involving aromatic[3-5] and olefinic π bases[6] as the proton acceptor. Furthermore, the differences between acetylenes and allenes as the proton acceptor are discussed in relation to their electronic states.

Experimental Section

Materials. 2,4-Dimethyl-2,3-pentadiene, Aldrich Chemical Co., was used. The other allene derivatives were prepared by treatment of the corresponding 1,1-dibromocyclopropane derivatives with methyllithium,[12] which were obtained by addition of dibromo-

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