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ON THE AROMATICITY OF ANNULENONES*

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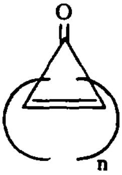
Abstract—Application of our method of predicting aromaticity‡ shows that the behavior of the annulenones is intermediate between that of the fulvenes (a nonaromatic series) and the annulenes (a series with strong alternation between aromatic and antiaromatic).

WE HAVE recently shown that a new treatment of the simple HMO results of conjugated hydrocarbons allows the prediction of aromaticities which correlate extremely well with the experimental properties of both alternant and nonalternant hydrocarbons.[1] Here we extend our approach to cyclic systems containing heteroatoms and calculate resonance energies of the annulenones (**1**),[2] a series of considerable recent interest.[2-10]



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Evaluation of $h_{\dot{O}}$ *and* $k_{C=O}$

Application of the simple HMO method to conjugated systems which contain heteroatoms requires appropriate changes in the coulomb and the resonance integrals. Equations 1 and 2 indicate how these changes are normally made. Although there are a number of values of $h_{\dot{O}}$ and $k_{C=O}$ available from previous

$$\alpha_{\dot{O}} = \alpha_C + h_{\dot{O}}\beta \quad (1)$$

$$\beta_{C=O} = k_{C=O}\beta \quad (2)$$

work,[11] the majority of these for the carbonyl oxygen were determined using the eigenvectors and/or excited state properties. Since resonance energies are a ground state property and arise from the eigenvalues, we sought a method for the determination of $h_{\dot{O}}$ and $k_{C=O}$ which would be based on a ground state property and would make use of the eigenvalues rather than the eigenvectors.

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‡ B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.* **93**, 305, (1971).

Our recent success in the calculation of heats of atomization, ΔH_a, of conjugated hydrocarbons using only the simple HMO method[12] indicated that these might be a suitable ground state property for the evaluation of $h_{\dot{O}}$ and $k_{C=O}$. Equation 3 was used to calculate hydrocarbon heats of atomization[12]

$$\Delta H_a = -(n_{CC}E_{CC} + n_{CH}E_{CH} + P\cdot\beta) \quad (3)$$

where n is the number and E is the energy of the indicated bond and $P\cdot\beta$ is the π-binding energy. The values of E_{CC}, E_{CH} and β were determined using equation 3 and the observed heats of atomization for a series of conjugated cyclic hydrocarbons utilizing the least squares method. The values obtained for E_{CC}, E_{CH} and β were $-3{\cdot}48543$ eV, $-4{\cdot}27606$ eV and $-1{\cdot}33077$ eV, respectively.*

A similar treatment of carbonyl compounds requires an additional bond energy term, $E_{C=O}$ (Eq 4). Ten compounds were chosen (Table 1) for

$$\Delta H_a = -(n_{CC}E_{CC} + n_{CH}E_{CH} + n_{C=O}E_{C=O} + P\cdot\beta) \quad (4)$$

which thermodynamic data were available[13] and their ΔH_a's fitted to Eq 4 by the least squares method. The previously obtained E_{CC} and E_{CH} values were used. Unlike the hydrocarbon case (Eq 3), the π-binding energy, $P\cdot\beta$, can be varied by variation of $h_{\dot{O}}$ and $k_{C=O}$. This was done in a systematic manner until a minimum for the square root of the sum of squares of the differences between the observed and calculated ΔH_a's (σ) was found. Unlike the cases of the amine nitrogen and the ether oxygen[14] an overall minimum of σ was found using the Pattern Search technique.[15]

TABLE 1. HEATS OF ATOMIZATION OF CONJUGATED COMPOUNDS CONTAINING CARBONYL OXYGEN

Compound	Heat of Atomization eV (25°) Observed	Calculated	Error
Formaldehyde	15·65	15·60	0·05
Glyoxal	26·74	26·78	−0·04
Benzaldehyde	68·51	68·50	0·01
p-Benzoquinone	60·04	60·15	−0·11
Benzophenone	121·10	121·36	−0·26
Benzil	132·32	132·48	−0·16
1,4-Naphthoquinone	94·15	94·07	0·08
9,10-Anthroquinone	128·21	127·99	0·22
5,12-Tetracenequinone	161·81	161·70	0·14
Tropone	67·98[a]	68·02	−0·04

[a] Ref. 22, corrected for strain as in ref. 12.

The values of the parameters at the minimum σ were $h_{\dot{O}} = 0{\cdot}22$ and $k_{C=O} = 0{\cdot}99$. These values were used in all subsequent calculations. The value of β was $-1{\cdot}3518$ eV and $E_{C=O}$ was $-1{\cdot}32997$ eV. We note here that this treatment of heats of atomization when carried out without tropone gave approximately the same error at the minimum σ but quite different values of $h_{\dot{O}}$ and $k_{C=O}$ as well as a poor value of the heat of atomi-

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* These values differ slightly from those previously obtained[12] as revised values[13] for ΔH_a were used.

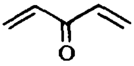
zation of tropone. This may be due to the lack of a really sufficiently wide and varied number of compounds. Hence, we note the desirability of additional thermodynamic data on conjugated carbonyl compounds to check further this method of obtaining the heteroatom parameters.

Evaluation of empirical carbonyl bond energy

To obtain resonance energies of the annulenones an empirical localized π bond energy for the carbonyl bond, $E^{\pi}_{C=O}$, is required. Once $E^{\pi}_{C=O}$ is obtained, then the localized π-binding energies of the cyclic compounds can be obtained using equation 5 where n_{ij} and E^{π}_{ij} are the number of and π-bond energy of the ij carbon–carbon

$$\text{Localized } \pi\text{-binding energy} = n_{C=O}E^{\pi}_{C=O} + \Sigma n_{ij}E^{\pi}_{ij} \qquad (5)$$

type.[1] $E^{\pi}_{C=O}$ was evaluated by a least squares fit of the HMO π-binding energies of the nine acyclics **2–10** (obtained with $h_{\dot{O}} = 0{\cdot}22$ and $k_{C=O} = 0{\cdot}99$) to Eq 5. The values of E^{π}_{ij} previously obtained[1] were used and $E^{\pi}_{C=O}$ was found to be $1{\cdot}9965\beta$.



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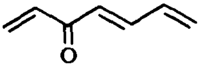

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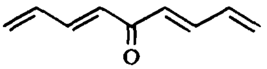

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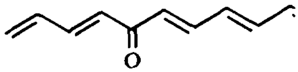

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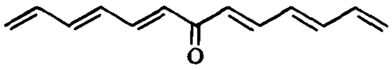

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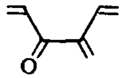

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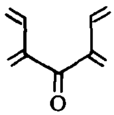

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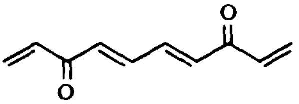

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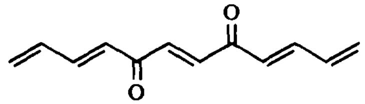

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In Table 2 are listed the Hückel π-binding energies, additive π-energies (from Eq 5) and the differences between the two for compounds **2–10**. Note the very small differences between the Hückel and additive energies for the nine compounds. This indicates the Hückel π-binding energies of the acyclics **2–10** are indeed additive as were the acyclic conjugated hydrocarbons.[1a]

Table 2. π Energy in units of β of acyclic ketones **2–10**

Compound	Hückel	Additive[a]	Dif	Dif/π electron (REPE)
2	6·901	6·869	0·032	0·005
3	9·413	9·405	0·008	0·001
4	11·924	11·941	−0·017	−0·002
5	14·452	14·476	−0·024	−0·002
6	16·981	17·013	−0·032	−0·002
7	9·333	9·305	0·028	0·004
8	11·764	11·740	0·024	0·002
9	14·361	14·344	0·017	0·001
10	16·853	16·888	−0·027	−0·002

[a] π energy calculated in an additive manner using the eight values of C—C π energies in Table 1 of ref. 1a and $E^{\pi}_{C=O}$.

The annulenones

π-Binding energies (with $h_{\dot{O}}$ = 0·22 and $k_{C=O}$ = 0·99) were calculated for the nine annulenones (**1**, *n* = 1–9). The localized or additive π-binding energies were also obtained using the C–C empirical bond energies in Table 1 of Ref 1*a*, $E^{\pi}_{C=O}$, and Eq 5. The difference between these two energies is the resonance energy. These results and resonance energy per π electron are listed in Table 3 for the annulenones.

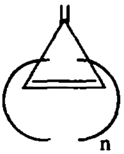
Table 3. Resonance energies in units of β of the annulenones

n	Hückel	Additive	RE	REPE
1	5·065	4·939	0·126	0·032
2	7·381	7·475	−0·094	−0·016
3	10·064	10·011	0·053	0·007
4	12·476	12·546	−0·070	−0·007
5	15·125	15·082	0·043	0·004
6	17·573	17·618	−0·045	−0·003
7	20·202	20·154	0·048	0·003
8	22·669	22·690	−0·021	−0·001
9	25·284	25·226	0·058	0·003

Most noteworthy of the results in Table 3 is that only the first two members of the series, cyclopropenone and cyclopentadienone, have resonance energies which are greatly different from zero (nonaromatic). Cyclopropenone is predicted to be aromatic. Breslow's recent synthesis of cyclopropenone and its high degree of stability relative to that or cyclopropanone[3] are indeed suggestive of its aromatic stabilization. On the other hand cyclopentadienone is predicted to be antiaromatic in agreement with its well established behavior. Until recently it had never been prepared and isolated in its monomeric form.[4,6] Its stability appears to be even less than might be expected of a nonaromatic compound since its dimer, dicyclopentadienone does not crack thermally to give cyclopentadienone but loses carbon monoxide instead. The failure of dicyclopentadienone to crack thermally may be contrasted to the similar dicyclotentadiene which does crack readily at a temperature well below that required for thermal expulsion of carbon monoxide in dicyclopentadienone.[16] The recent synthesis of cyclopentadienone has added further evidence of its high instability since, although it is stable indefinitely at −196°, it undergoes dimerization below −80°.[9] Hence both our calculations and the above experimental evidence are indicative of cyclopentadienone's *antiaromaticity.*

The degree of aromaticity of the next member in the series, tropone, has been controversial over the years. Earlier workers expected it to be aromatic, but recent experimental evidence[17, 18] suggests that tropone is polyene- or polyenone-like in its behavior. After an examination of the dipole moment, bond lengths and proton coupling constants of this molecule, Bertelli *et al.*[18] concluded, "that the dipolar character of tropone has been greatly overestimated and that tropone exhibits properties closely resembling those of a polyenone." This is in agreement with our computed REPE of $0{\cdot}007\ \beta$ which indicates that it is essentially polyene- or polyenone-like in its behavior. It should have only a very small degree of aromatic stabilization, or stating it in another way, tropone lies in the borderline region between nonaromatic and aromatic. It is perhaps this borderline nature of tropone which has led to the controversy over its aromaticity. That is, it displays some properties which are indicative of a nonaromatic compound, for example bond length alternation, and others which are indicative of an aromatic compound, for example its inability to form a 2,4-dinitrophenylhydrazone. Dewar and Bertelli have found tropone to be nonaromatic by more complex methods of calculation.[7, 19] The remainder of the series (Table 3) are all predicted to be polyenone-like in their behaviour.

The behaviour of the annulenones appears to be intermediate between the two related monocyclic series, the annulenes and the fulvenes (11). Fulvenes, the hydrocarbon analogues of the annulenones show no alternation between aromatic and nonaromatic whereas the annulenes show a high degree of alternation with the convergence to nonaromaticity coming considerably later in the series than in the annulenones (Fig. 1). The limiting REPE of the annulenes may be found by summing the closed form for orbital energies[20] over filled orbitals using Gradshteyn and Ryzhik's[2] formula 1.342.2. Taking the limit as the number of C atoms increases gives. in the notation of Ref 1, REPE $= 4/\pi - \frac{1}{2}(E^{\pi}_{22} + E^{\pi}_{12}) = 0{\cdot}0053\beta$.



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Finally, some comment should be made about the expected accuracy of our predictions. For unstrained hydrocarbons we have shown[12] REPE to be accurate to $\pm 0{\cdot}004\ \beta$. We cannot be certain that the REPE's for the oxygen containing compounds

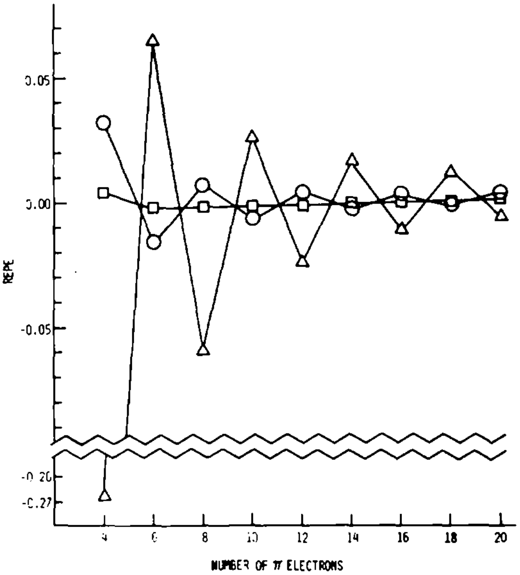

FIG 1. Resonance energies per π electron (REPE) in units of β of the annulenes (△), annulenones (○) and fulvenes □) *vs* the number of the π electrons.

of the present paper are that good. The average error in the computed heats of atomization in Table 1 is 2·6 kcal/mole. The accuracy of the experimental heats of atomization is of this magnitude so that we do not know whether the discrepancy is due to experimental error or to failure of the Hückel computations. Note that this average error in computed heat of atomization by our simple method is very nearly the same as Dewar's error of 2·5 kcal/mole for oxygen compounds (Table VII of Ref 7) using more elaborate methods. In either case the error is large compared to our computed annulenone resonance energies. For example, the total resonance energy of cyclopropenone is 3·9 kcal/mole. We might hope that a part of the error would cancel in taking the difference in energy between a molecule and its reference structure and that therefore resonance energies would have great accuracy than heats of atomization. We cannot be sure that this is so, but the agreement between predicted and observed properties discussed above seems to support our expectation.

REFERENCES

[1] [a] B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.* **93**, 305 (1971);
[b] B. A. Hess, Jr., and L. J. Schaad, *Ibid.* **93**, 2413 (1971);
[c] B. A. Hess, Jr., and L. J. Schaad, *J. Org. Chem.* **36**, 3418 (1971);
[d] B. A. Hess, Jr., and L. J. Schaad, *Tetrahedron Letters* **17** (1971)
[2] G. M. Pilling and F. Sondheimer, *J. Am. Chem. Soc.* **90**, 5610 (1968).
[3] R. Breslow, G. Ryan, and J. T. Groves, *Ibid.* **92**, 988 (1970)
[4] C. H. DePuy, M. Isaks, K. L. Eilers, and G. F. Morris, *J. Org. Chem.* **29**, 3503 (1964)
[5] E. W. Garbisch, Jr., and R. F. Sprecher, *J. Am. Chem. Soc.* **91**, 6785 (1969)
[6] W. Grimme, J. Reisdorff, W. Jünemann, and E. Vogel, *Ibid.* **92**, 6335 (1970)

[7] M. J. S. Dewar, A. J. Harget and N. Trinajstić, *Ibid.* **91**, 6321 (1969)

[8] N. Trinajstić, *Record of Chemical Progress* **32**, 85 (1971)

[9] O. L. Chapman and C. L. McIntosh, *Chem. Commun.* 770 (1971)

[10] H. Ogawa, N. Shimojo and M. Yoshida, *Tetrahedron Letters* 2013 (1971)

[11] W. P. Purcell and J. A. Singer, *J. Chemical and Engineering Data* **12**, 235 (1967)

[12] L. J. Schaad and B. A. Hess, Jr., *J. Am. Chem. Soc.* **94**, 3068 (1972)

[13] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds.* Academic Press, New York (1970)

[14] B. A. Hess, Jr., L. J. Schaad and C. W. Holyoke, Jr. *Tetrahedron* **28**, 3657 (1972)

[15] D. J. Wilde, *Optimum Seeking Methods* p. 145. Prentice-Hall, Englewood Cliffs, N.J., (1964)

[16] C. H. DePuy and C. E. Lyons, *J. Am. Chem. Soc.* **82**, 631 (1960)

[17] D. Lloyd, *Carbocyclic Non-Benzenoid Aromatic Compounds.* p. 120, Elsevier, Amsterdam (1966)

[18] D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, *J. Am. Chem. Soc.* **91**, 5286 (1969)

[19] D. J. Bertelli and T. G. Andrews, Jr., *Ibid.* **91**, 5280 (1969)

[20] C. A. Coulson and A. Streitwieser, Jr., *Dictionary of π-Electron Calculations*, p. XXX. Freeman, San Francisco, California (1965)

[21] I. S. Gradshteyn and I. M. Rhyzhik, *Tables of Integrals, Series, and Products*, p. 30. Academic Press, New York (1965)

[22] W. Jackson, T. S. Hung, and H. P. Hopkins, Jr. *J. Chem. Thermodynamics*, 347 (1971)