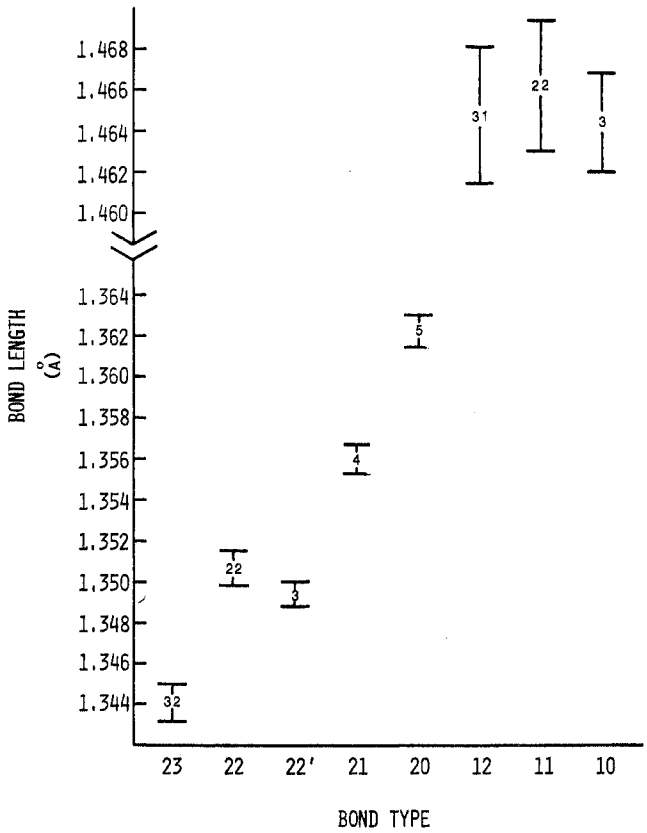

Figure 1 .—Calculated bond lengths[1,11] in acyclic hydrocarbons. The bond types are those in Table I. The numbers between bars give the number of bonds of a type in the indicated range (*e.g.*, there are 32 bonds of type 23 computed to have length between 1.343 and 1.345 Å). Note the break in scale between 1.36 and 1.46 Å.

indeed these terms can be used to obtain the π energies of linear acyclic polyenes, they do not give additivity for many branched acyclic polyenes (see Table II).

TABLE II

COMPARISON OF ADDITIVITY OF BRANCHED ACYCLIC POLYENES USING TWO AND EIGHT BOND TYPES WITH THE HÜCKEL AND LCAO-BETA METHODS

	Hückel REPE (β)		LCAO-BETA REPE (eV)	
Compd	Two bond types[a]	Eight bond types[b]	Two bond types[c]	Eight bond types[d]
	−0.024	0.004	−0.012	0.004
	−0.029	0.003	−0.021	0.003
	−0.016	0.001	−0.011	0.001

[a] Bond energies in ref 9 used. [b] Reference 4. [c] Bond energies in ref 10 used. [d] Eight bond energies obtained using LCAO-BETA energies of 40 acyclics in ref 4.

Hence a basic premise of Dewar's definition—the additivity of all acyclic polyenes—does not hold. Furthermore, a comparison of our HMO resonance energies per π electron (REPE) with Trinajstić's aromatic stability per π electron (A_s/e) (see Table III) indicates that while for many compounds the two methods give very similar results there are notable exceptions. The REPE of fulvene suggests that it is nonaromatic, while

TABLE III

HÜCKEL RESONANCE ENERGY PER π ELECTRON (REPE), INDICIES OF AROMATIC STABILITIES PER π ELECTRON (A_s/e), AND LCAO-BETA RESONANCE ENERGIES PER π ELECTRON (LCAO-BETA REPE)

Registry no.	Compd	REPE (β)	A_s/e (β)	LCAO-BETA REPE (eV)[a]
71-43-2	Benzene	0.065	0.073	0.075
91-20-3	Naphthalene	0.055	0.056	0.064
129-00-0	Pyrene	0.051	0.049	0.060
83-32-9	Acenaphthalene	0.039	0.038	0.047
275-51-4	Azulene	0.023	0.024	0.027
3227-90-5	Trimethylenecyclopropane	−0.002	−0.043	−0.001
497-20-1	Fulvene	−0.002	−0.016	−0.002
250-25-9	Pentalene	−0.018	−0.018	−0.020
5291-90-7	Dimethylenecyclobutene	−0.028	−0.058	−0.028
6249-23-6	Calicene	0.043	0.043	0.050
4026-23-7	Benzocyclobutadiene	−0.027	−0.027	−0.020
4095-06-1	Methylenecyclopropene	0.005	−0.020	0.005

[a] Obtained using eight bond-energy terms calculated from the energies of the 40 acyclics in ref 4.

the A_s/e indicates that it is antiaromatic. The same is true for methylenecyclopropene and trimethylenecyclopropane.

The LCAO-BETA Method of Figeys.—Using an iterative method to adjust the Hückel parameters Figeys has also determined that the energies of the linear acyclic polyenes are additive when only two bond energy terms are considered and has used these terms to obtain resonance energies of the annulenes.[10] However, as in the simple Hückel method, we have found that these terms do not give accurate additivity of branched acyclic polyenes (see Table II). We have carried out a treatment of the LCAO-BETA results in a fashion exactly analogous to our treatment of the simple Hückel results.[4] One is able to obtain eight bond-energy terms which do give additivity of all acyclic polyene energies. Furthermore, resonance energies obtained with these terms are almost exactly analogous to the Hückel resonance energies obtained by our method (Table III). Hence it appears that nothing is gained over the simple Hückel method in going to the more complex LCAO-BETA method.

Heterocycles Containing a d-Orbital Acceptor Atom. Consideration of the Dependence of Structural and Reactivity Effects on Whether the Number of Ring Atoms Is Odd or Even

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I wish to call attention to a ring-size effect upon the symmetry of planar cycloalkane filled molecular orbitals. The effect is such that heterocycles containing

a d-orbital acceptor atom in the ring are predicted to show properties which depend on whether the ring size is odd or even.

The extension of the Walsh formulation of cyclopropane molecular orbitals to cyclobutane has recently been discussed.[1] Orbitals for planar rings of larger size may be similarly constructed from sp^2 carbon atoms. The overlapping sp^2 orbitals within the ring are analogous to the orbitals for cyclic π sytems. The energies for such orbitals may be obtained by inscribing a polygon with vertex *down* in a circle with radius equal to the energy of the most bonding orbital.[2] Coefficients of the orbitals are sine or cosine functions of appropriate angles.[2]

A second set of orbitals results from the overlap of the p orbitals outside the ring. Whereas the inside orbitals always exhibit one all-bonding combination, outside orbitals have a possible fully antibonding combination. Furthermore, the alternation of positive and negative lobes leads to other outside molecular orbitals having antibonds corresponding to the *bonds* of inside molecular orbitals.[2c] Accordingly, the energies of the outside molecular orbitals are represented by inscribing a polygon with vertex *up* in a circle whose radius is the energy of the fully antibonding orbital.[2c] Coefficients for the unoccupied inside orbitals become those for occupied outside orbitals.[2c]

In Figure 1 occupied orbitals and their symmetries with respect to *yz* and *xz* planes (the plane of the paper is *xz*) are shown for ring sizes 3, 4, 5, and 6. Replacement of the carbon atom at the bottom vertex of each ring by a d orbital containing electronegative heteroatom will cause the filled ring orbitals to mix with the vacant d orbitls of the same symmetry, leading to a decrease of the energy of the electron pair. Since there are two d orbitals of Ss symmetry and only one of As symmetry, the ring Ss orbitals are subject to a double decrease and may be stabilized to a greater extent than ring As orbitals which are subject to a single decrease. Odd-sized rings, in which the number of Ss orbitals exceed by one the number of As orbitals may, accordingly, be stabilized in comparison with even-sized rings and may have more electron density displaced from the ring to the heteroatom. (The d_{xy} and d_{yz} orbitals, having Aa and As symmetry, respectively, do not interact with ring orbitals.) The more difficult to evaluate overlaps and energy differences between the mixing orbitals also must be considered, suggesting that resort to experimental data be made for possible verification of odd–even effects.

Although ^{13}C nmr data for cyclic sulfides (Table I, column 2) provide some evidence for the odd–even effect, the phenomenon is expected to be most pronounced for molecules in which the heteroatom is positively charged. In Table I we cite data for cyclic halonium and sulfonium ions which suggest that the

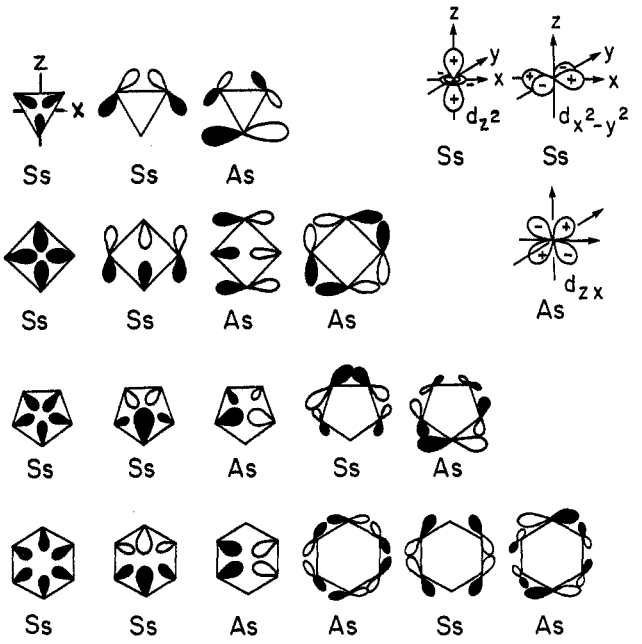
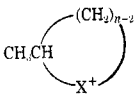
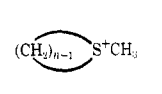
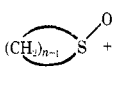


Figure 1.—Cycloalkane Walsh type filled molecular orbitals and the d-acceptor orbitals of the same symmetries.

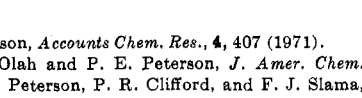
TABLE I

CHEMICAL SHIFT DATA FOR CYCLIC SULFIDES, RATE DATA FOR TRIFLUOROACETOLYSIS OF CHLOROALKYL *p*-NITROBENZENESULFONATES, RATES OF H–D EXCHANGE IN CYCLIC METHYLSULFONIUM IONS, AND PER CENT REDUCTION OF CYCLIC SULFOXIDES BY SODIUM HYDROGEN SULFITE

Ring size, *n*	$\Delta\delta,\alpha$-^{13}C cyclic sulfide[a]	Estd $k\Delta$[b] to give 	Rel *k*, α-ring H[c] 	Rel *k*, H in CH_3-S^+[c] 	% redn, 60 min,[d]
3	21.5	0.09			
4	4.4	<0.0003[e]	<2.5[f]	770[f]	18
5	6.2	52	20	4.6	100
6	1.8	1.4	1.2	7.3	16
7		0.065	12	3.1	52
Cyclic			0.7–1.9[g]	3.7–6[g]	

[a] Difference between the α-carbon chemical shift and that of the cycloalkane of the same ring size: G. E. Maciel and G. B. Savitsky, *J. Phys. Chem.*, 69, 3925 (1965). [b] Reference 5, 10^5k, sec^{-1}. [c] Reference 9. [d] Reference 10. [e] <5% of k_{total} based on data for the trifluoromethanesulfonate.[6] [f] For the β,β-dimethyl compound. [g] Range for diethyl, dipropyl, diisopropyl, and diisobutylmethyl sulfonium salts.[9]

effect is observable for ring sizes beyond those where planarity is expected. Cyclic three-membered and five-membered chloronium, bromonium, and iodonium ions are well known, both as stable species in SbF_5–SO_2 and as reaction intermediates obtained by neighboring-group participation.[3] However, attempts to obtain six-membered species have led exclusively to five-membered rings (eq 1).[4] Under solvolytic con-



(1)

(1) R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971), and references cited therein.

(2) (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 47, 257. (b) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, pp 113–118. (c) A mathematical demonstration that the orbitals and their coefficients are those described here will appear following these pages in the microfilm edition of this journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-4180. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(3) P. E. Peterson, *Accounts Chem. Res.*, **4**, 407 (1971).

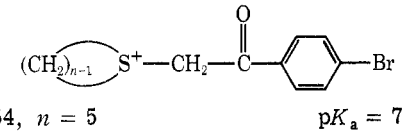
(4) (a) G. A. Olah and P. E. Peterson, *J. Amer. Chem. Soc.*, **90**, 4675 (1968); (b) P. E. Peterson, P. R. Clifford, and F. J. Slama, *ibid.*, **92**, 2480 (1970).

ditions partial formation of a five-membered ring apparently occurred during an attempt to obtain an intermediate six-membered ring in solvolysis of 5-chloro-1-hexyl *p*-nitrobenzenesulfonate.[5] A similar attempt to obtain a four-membered-ring iodonium ion intermediate apparently gave partial formation of the three-membered ring.[6] Furthermore, numerous attempts to obtain stable four-membered halonium ions in SbF_5–SO_2 led exclusively to three- and five-membered rings or both.[7]

Rate data (Table I, third column) emphasize the preference for three- and five-membered-ring halonium ion formation in solvolysis reactions, although participating groups not having d orbitals show a substantially similar pattern.[8] In the case of cyclic sulfonium ions, recently published rates of base-catalyzed hydrogen-deuterium exchange (Table I) provide striking odd–even effects.[9] Electron transfer from the five- and seven-membered ring carbons to sulfur can account for the increased exchange rate of the endocyclic α hydrogens. For the four- and six-membered rings electron transfer from the methyl group is facilitated, since the endocyclic orbitals are relatively ineffective in filling the d orbitals.

The last column in Table I gives data for per cent reduction of cyclic sulfoxides to cyclic sulfides by sodium hydrogen sulfite.[10] The data suggest that the rate of reduction shows alternation as ring size is incremented, althouth detailed interpretation of the multistep mechanism would be premature.

Finally, we note that pK_a data for the protonated form of sulfur containing ylides,[11] shown below, is consistent with the H–D exchange results in Table I, in that protons exocyclic to six-membered S-containing rings are more acidic than those of the comparable five-membered-ring compound.



$pK_a = 7.54$, $n = 5$ $pK_a = 7.00$, $n = 6$

The consideration mentioned above suggests a plethora of interesting experiments and theoretical investigations, covering a range of heterocycles incorporating d-orbital atoms. Several referees have pointed out that the magnitude of the interactions mentioned in this paper may be too small to dominate the chemistry of such heterocycles. However, we feel that consideration of the proposed orbital effect should be made in conjunction with studies of such heterocycles, and we accordingly present the concept in its present form. Even greater generality would obtain if the well-known general difficulty of obtaining four-membered rings[8] could be incorporated into our correlation. Possible selective stabilization of electron pairs in odd-ring orbitals having orbital dipole moments and/or large coefficients at the heteroatom deserve investigation.

Acknowledgment.—Support by the National Science Foundation (Grant GP 30684) is gratefully acknowledged. We are grateful for a discussion with Dr. B. M. Gimarc.

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(8) *Cf.* E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 104.
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Spectroscopic Differences between Crystalline and Amorphous Phases of Indigo

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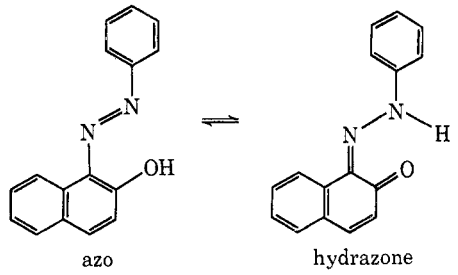
The vacuum evaporation of organic molecules has been used by a number of workers as a method of producing a desired polymorphic phase of the material.[1] It has been found for some organic systems that the amorphous state is initially formed upon vacuum evaporation and that the amorphous organic state is surprisingly stable under ambient conditions for periods ranging from days to years.[2] Of major interest are the wide variations in both spectral and electrical properties between the crystalline and amorphous phases of a given organic compound.[2] For example, the trans hydroxyazo aromatics show profound differences between the preferred species in the amorphous solid state and the crystalline phases. The lowest energy electronic transition of crystalline hydroxyazo compounds is red shifted ~1000 Å relative to that for the amorphous solid state or fluid media. This anomalous absorption characteristic of the crystalline phase has been attributed to intermolecularly hydrogen bonded hydrazone aggregates, whereas the amorphous state and solution state have been identified as being composed of a hydrazone–azo tautomeric equilibrium.[3]



azo hydrazone

Indigo has also been reported[4] to show visible absorption at considerably longer wavelengths (600–700 Å) in the solid phase than in organic solvents. From the electronic spectral observations and supporting

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