


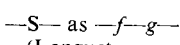
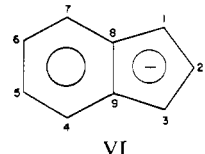
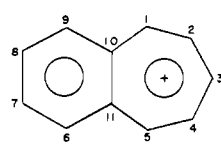
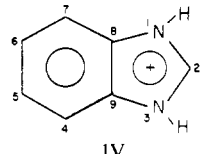
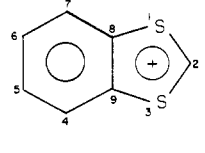




**Table I. Parameter Values Used in  $\omega$ -Technique Calculations**

Heteroatom X or Y	$h_x$	$k_{cx}$	$\delta_{c'x}$	Reference
	1.5	0.8	0.15	Streitwieser, p. 135 (1961)
	2.0	0.8	0.2	Streitwieser, p. 135 (1961)
	1.0	0.7	0.1	Zahradnik, p. 10 (1965) } $k_{cx}$ is an average of those in Zahradnik (1965)}
 (Longuet-Higgins)	$h_f = 0$ $h_g = 0$	$k_{cf} = 0.7$ $k_{cg} = 0.7$ $k_{fg} = 1.0$	...	Zahradnik, p. 9 (1965) } $k$ values are averages of those in Zahradnik (1965)}
	$\omega = 1.4$			Ettinger (1964) Kier and Roche (1966)

**Table II. Some Previous Calculations of Benzodiheterolium Ions**

System	Position	Charge Density	Bond	Bond Order	Reference and Notes	
 VI	1	1.251	1-2	0.659	Streitwieser and Brauman (1965)	
	2	1.111	1-8	0.565		
	6	1.059	5-6	0.595		No. 9.2.5.53
	7	1.034	6-7	0.723		Simple Hückel
	8	1.098	7-8	0.553		
				8-9		0.486
 X	1	0.813	1-2	0.673	Streitwieser and Brauman (1965)	
	2	0.921	1-10	0.550		
	3	0.818	2-3	0.629		No. 11.2.6.94
	8	0.953	7-8	0.601		Simple Hückel
	9	0.969	8-9	0.716		
	10	0.932	9-10	0.561		
 IV	1	1.52			Brown and Heffernan (1956)	
	2	0.81				
	6	1.03				Simple Hückel with $h_N = 1.0$
	7	1.03				
	8	1.01				
 V	a) 1	1.739	1-2	0.584	Zahradnik <i>et al.</i> (1960)	
	2	0.704	1-8	0.467		
	6	0.970	5-6	0.622		Simple Hückel with overlap using Longuet-Higgins model for sulfur
	7	0.986	6-7	0.704		
	8	0.953	7-8	0.601		
			8-9	0.534		
	b) 1	1.796	1-2	0.507		$S_{cc} = S_{ss} = 0.25$ $S_{cs} = kS_{cc}$ a) $k = 0.6$ b) $k = 0.8$
	2	0.526	1-8	0.343		
	6	0.981	5-6	0.641		
	7	0.989	6-7	0.684		
8	0.971	7-8	0.627			
		8-9	0.594			

(1960) are not in agreement with the simple Hückel calculations used to initiate the  $\omega$ -technique calculations in this study because of the different choice of parameters.

The total  $\pi$ -energy, the Wheland localization energy, and the charge density on C-2 are given in Table III. For ease of discussion the cations are grouped in this table in the following way. Group 1 consists of cations in which both heteroatoms are the same. In Groups 2 through 5

one of these heteroatoms, X, is kept constant while the other, Y, is varied.

#### DISCUSSION

These studies indicate that there has been a shift of  $\pi$ -electrons from the six- to the five-membered ring. The size of this shift varies with the systems studied ranging from 0.02 to 0.30 electron, as seen from the charge



Table III. Energies and Charge Densities

Group	Cation	Total $\pi$ Energy, $\beta$	Wheland Loc. Energy, $\beta$	Charge Density, $q_2$
1	X	15.947	3.083	0.850
	IV	18.142	3.203	0.722
	III	19.892	2.959	0.674
	V	15.998	3.174	0.745
	V-A	14.599	2.170	0.745
2	XII	17.045	3.133	0.815
	IV	18.142	3.203	0.722
	VIII	19.021	3.084	0.704
	IX	17.068	3.187	0.734
	IX-A	16.369	2.675	0.739
3	XI	17.912	3.011	0.812
	VIII	19.021	3.084	0.704
	III	19.892	2.959	0.674
	VII	17.963	3.083	0.715
	VII-A	17.217	2.352	0.717
4	XIII	15.995	3.135	0.821
	IX	17.068	3.187	0.734
	VII	17.963	3.083	0.715
	V	15.998	3.174	0.745
	4-A	XIII-A	15.290	2.645
	IX-A	16.369	2.675	0.739
	VII-A	17.217	2.352	0.717
	V-A	14.599	2.170	0.745
5	X	15.947	3.083	0.850
	XII	17.045	3.133	0.815
	XI	17.912	3.011	0.812
	XIII	15.995	3.135	0.821
	XIII-A	15.290	2.645	0.815

larger the electron density at C-2 indicating a greater delocalization. In each group the  $q_2$  values in ions where Y is N or S are close to each other and greater than the  $q_2$  value in the ion where Y is O. For example, in Group 2 of Table III  $q_2$  for cation VIII is 0.704 while for cations IV and IX it is 0.722 and 0.734, respectively. Thus, from the aspect of charge densities on the cation, electron or hydride acceptor activity at C-2 in cations where Y is O is expected to be greater than when Y is N or S (Hennessy, 1965).

Since equilibria studies involve products and reactants, the  $\pi$ -energy of the benzodiheteroline being formed must also be considered in some way when discussing reactivity. Wheland localization energies for C-2 afford one way of doing this and show the same order of reactivity toward electron or hydride donors (Brown, 1952; Wheland, 1942). The similarity between the formation of a Wheland intermediate and a benzodiheteroline formed from the corresponding cation is noted in Figure 2.

The smaller the localization energy for the positive charge at C-2, the greater the ease of hydride acceptance at this site. These localization energies vary in all but one of the groups in the following order: O  $\ll$  S < N. Group 5 of Table III is the exception, where X is C=C. This order of localization energies shows oxygen-containing cations as more reactive toward hydride donors than the corresponding sulfur- or nitrogen-containing species. The nitrogen-containing species are least reactive. This reflects the order of synergistic activity found experimentally among the benzodiheterolines (Hennessy, 1966).

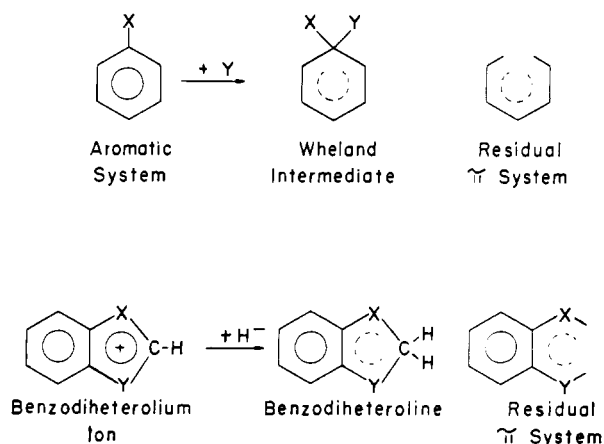


Figure 2. Comparison of Wheland intermediate and benzodiheteroline formed from benzodiheterolium cation

Thus, the isolated molecule approximation—i.e., the use of charge densities—and localization theory are in accord with Brown's rules (1952) in predicting C-2 to be the position of greatest electron or hydride acceptor activity. This has been shown experimentally for V and VII (Soder and Wizinger, 1959a,b; Wizinger and Durr, 1963).

The use of the Longuet-Higgins model places more electron density on sulfur than do calculations in which d-orbital participation is neglected. This increase is such that within each group there is a greater electron density on the Y = S atom than on the Y = O atom of the related compound. For example, in Figure 1, in comparing benzoxazolium (VIII) with benzothiazolium (IX-A) the charge density on the sulfur in IX-A is greater than the charge density on the oxygen in VIII. It is unlikely that this actually is the case. This reflects the difficulty of incorporating d-orbital participation in the sulfur  $\pi$ -bonds by means of the Longuet-Higgins model in a simple  $\omega$ -technique calculation (Orloff, 1963).

Values for the lowest empty molecular orbital (LEMO) resulting from the  $\omega$ -technique calculations are given in Table IV. The four oxygen-containing cations have positive LEMO orbital energies. As such, these are ready electron acceptors. With electron donors of low highest occupied molecular orbital energies they may readily form charge transfer complexes (Nepras and Zahradnik, 1964).

Table IV. Orbital Energies of Lowest Empty Molecular Orbitals in Units of  $\beta$ , Bonding Orbitals Have Positive Values

Cation	LEMO
III	0.165
IV	-0.046
V	-0.124
VI	-1.004
VII	0.013
VIII	0.059
IX	-0.086
X	-0.055
XI	0.084
XII	0.009
XIII	-0.016

From the above discussion of the cation localization energies and charge densities at position 2, these simple molecular orbital calculations reinforce the postulated mechanism of hydride transfer. As noted previously (Hennessy, 1965), NAD<sup>+</sup> or NADP<sup>+</sup> could ultimately act as the hydride acceptor in the biological oxidation-reduction process. The localization energies also indicate the oxygen containing cations should be more effective in inhibiting the metabolism of certain pesticides than should the corresponding nitrogen or sulfur moieties.

Calculations using other parameter values and involving sigma electrons are now in process.

#### ACKNOWLEDGMENT

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