previously, adequately deal with nonplanar systems or with molecules containing large steric interactions in the σ system. It is possible, of course, to do an all valence electron calculation, but these are in general very lengthy, often prohibitively so, and still of some-

what questionable reliability. A better approach to the problem, the force field approach, will form the subject of a subsequent paper.[41]

Calculations on Quinonoid Compounds. I. The Quinododimethides

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Abstract: A series of 31 quinododimethides have been investigated by SCF molecular orbital calculations. No support can be found for earlier predictions that appreciable electron delocalization may be found for such nonbenzenoid systems. The relevance of quinododimethides to certain electrocyclic ring opening reactions is dealt with.

Current theory concerning electronic structure in polyolefinic compounds tends toward the conclusion that a slight, consistent delocalization is operative. Self-consistent field (SCF) calculations on branched polyolefins indicated that the total π energy was a simple sum of the contributing parts.[2,3] While the quinododimethides were not treated in these studies, it is plausible that only limited aromaticity is associated with these species.

Early calculations on the quinododimethides, however, were of the most simple type. These calculations, whether involving a Hückel molecular orbital or valence bond approach, were uniform in their predictions. Thus, Namiot, Dyatkina, and Syrkin determined appreciable resonance energies for 1,2- and 1,4-benzenequinododimethide by both methods.[4] The molecular orbital approach was also applied to the hypothetical 1,3-benzenequinododimethide. While predicted to possess less resonance energy than its two isomers, significant stabilization was claimed.[4] Coulson, Craig, Maccoll, and Pullman obtained results which tended to substantiate the above findings.[5] In the case of 1,4-benzenequinododimethide, a very low separation between the singlet and triplet structures was predicted by molecular orbital theory.[5] Dyatkina and Syrkin also calculated similarly low energy barriers for other quinododimethides, particularly for those systems where only a single classical structure can be drawn.[6]

Experimental findings tend to contradict the prediction of moderate stability for simple quinododimethides. Thus, for example, 1,2-benzenequinododimethide should be obtained from the thermal elimination of sulfur dioxide from 1,3-dihydroisothianaphthene 2,2-

dioxide. While the quinododimethide has been trapped as a Diels–Alder adduct with anthracene, it has resisted isolation.[7] A similar failure was noted in the attempts to prepare 1,4-benzenequinododimethide *via* pyrolysis of the *p*-methylbenzyl radical.[8] Even those systems in which the quinododimethide moiety should be stabilized by the annellation of benzene rings have not been isolated at room temperature. Eliminations from various precursors should yield 9,10-anthracenequinododimethide and 9,10-phenanthrenequinododimethide. Both can be trapped only as Diels–Alder adducts.[9,10]

Recent reconsiderations of HMO calculations also would indicate that the earlier results have exaggerated possible electron delocalization in related systems. Hess and Schaad have pointed out that in assigning the π energy of the hypothetical, localized reference structure as 2β/double bond without consideration of the nature of attached groups and, more importantly, by neglecting contributions to the π energy by formal single bonds, the total π energy of these structures may be seriously underestimated.[11] Subsequent recalculations of resonance energies as differences in π energy between those of HMO calculations and those newly determined for the reference state have produced results which nicely parallel the corresponding results of the SCF approach.[11,12] Unfortunately, the quinododimethides were again not considered.

In order to systematically study this class of compounds, we have carried out SCF calculations for the 31 quinododimethides shown in Figure 1. Two variants of the Pople–Pariser–Parr approach were utilized. The first was based upon fixed geometries in which a constant bond length (CBL) of 1.4 Å was employed. The second method allowed for the use of variable bond lengths (VBL) *via* incorporation of a bond order–bond

(1) NDEA Fellow, 1971–present.
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length relationship. At the end of each iteration new values of two-center electron repulsion integrals between bonded atoms and the corresponding resonance integrals were redetermined. Details may be found in the literature.[13] HMO CBL calculations were also carried out.

Resonance Energies

In Table I are presented the results of simple HMO

Table I. Results of HMO Calculations[a]

Compd	$E_{\pi b}$	$E_{\pi b}$ loc[b]	RE	REPE
1	9.954	9.9140	0.040	0.005
2	9.929	9.8846	0.044	0.006
3	15.802	15.4637	0.338	0.028
4	15.802	15.4637	0.338	0.028
5	15.532	15.4388	0.093	0.008
6	15.475	15.4094	0.065	0.005
7	21.483	20.9885	0.494	0.031
8	21.133	20.9636	0.169	0.010
9	21.481	20.9885	0.493	0.031
10	21.680	21.0428	0.637	0.040
11	21.524	21.0134	0.511	0.032
12	21.347	20.9885	0.359	0.022
13	21.517	21.0134	0.504	0.032
14	21.682	21.0428	0.639	0.040
15	21.511	21.0134	0.498	0.031
16	24.536	24.0362	0.500	0.028
17	24.539	24.0362	0.503	0.028
18	24.533	24.0317	0.501	0.028
19	24.749	24.0611	0.688	0.038
20	27.121	26.5133	0.608	0.030
21	26.741	26.4884	0.253	0.013
22	27.362	26.5676	0.794	0.040
23	27.208	26.5676	0.640	0.032
24	27.391	26.5925	0.799	0.040
25	27.439	26.5925	0.847	0.042
26	27.283	26.5631	0.720	0.036
27	27.272	26.5631	0.709	0.035
28	27.202	26.5676	0.634	0.032
29	27.312	26.5925	0.720	0.036
30	32.798	32.0381	0.760	0.034
31	32.351	32.0132	0.338	0.015

[a] All results given in β units. [b] As determined by the method of Hess and Schaad.[11]

calculations. The method and parameters of Hess and Schaad were used to determine the energies of localized structures. Both the directly obtained resonance energies and the resonance energy per electron (REPE) are tabulated. With one exception, the overall results are gratifying. The prototype systems, 1,2- and 1,4-benzenequinododimethide (**1** and **2**), have REPE values only slightly greater than most of the polyolefins investigated originally.[11] Annellation of benzenoid units to the basic structures produces a strongly stabilizing effect. This is particularly true for 9,10-anthracene-quinododimethide (**10**) and 9,10-phenanthrenequinodo-dimethide (**14**) where both the cyclic double bonds of the prototype have been incorporated into aromatic rings. The disturbing result concerns the series of 2,3-acenequinododimethides (**1, 5, 8, 21,** and **31**). Although but a single classical structure can be written for each of these molecules, there is a steady increase in REPE values. Thus, 2,3-pentacenequinododi-methide (**31**) is predicted to possess nearly half the "aromatic character" associated with pentacene itself
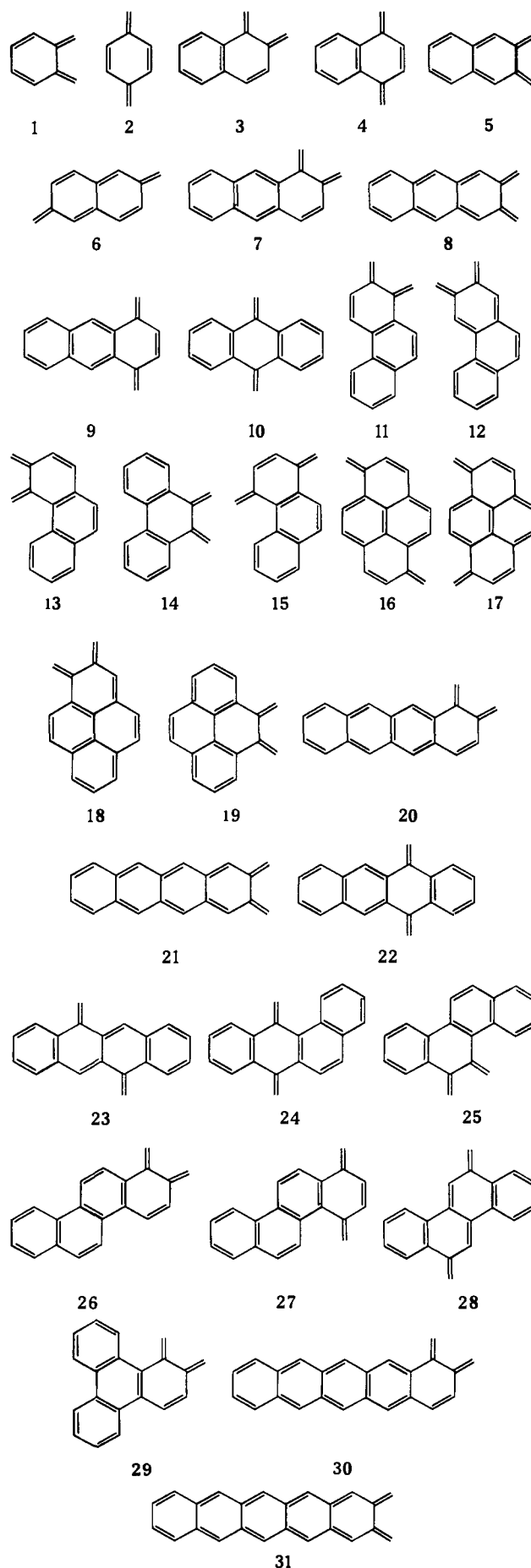
(13) M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 685 (1965).

Figure 1.

or 70% that of azulene. This seems particularly suspect.

Table II contains the corresponding results from our

Table II. Results of SCF CBL Calculations[a]

Compd	$E_{\pi b}$	RE
1	8.910	−0.881
2	8.710	−1.081
3	14.977	0.781
4	14.890	0.694
5	14.165	−0.852
6	13.769	−1.248
7	20.585	1.730
8	19.483	−0.759
9	20.530	1.675
10	21.076	2.475
11	20.658	1.803
12	20.176	0.755
13	20.663	1.808
14	21.116	2.515
15	20.533	1.678
16	23.455	1.822
17	23.466	1.833
18	23.524	1.891
19	24.223	3.157
20	26.042	2.528
21	24.818	−0.650
22	26.737	3.477
23	26.243	2.417
24	26.716	3.456
25	26.779	3.519
26	26.468	2.954
27	26.364	2.850
28	26.103	2.276
29	26.479	2.965
30	31.461	3.288
31	30.167	−0.526

[a] All results given in electron volts.

SCF CBL calculations. In obtaining resonance energies, the former approach of Dewar and Gleicher[2] was slightly modified. This was necessitated by the presence of benzenoid rings. The expression utilized was

$$E_R = N_Q'(E_Q^S - E') + N_Q''(E_Q^D - E'') - $$
$$(N_B'' + N_B')A + \frac{N_B' - N_B''}{2}(E'' - E') - E_{\pi b}$$

N_Q' and N_Q'' are the number of quinonoid or nonaromatic carbon–carbon single and double bonds, N_B' and N_B'' are the corresponding benzenoid bonds, E'' and E' are the total energies for double and single bonds between sp^2 hybridized carbon atoms, E_Q^S and E_Q^D are the σ energies of nonaromatic carbon–carbon single and double bonds, and A is a parameter based upon the average σ energy of an aromatic carbon–carbon bond.[13] Values for all terms have been published.[2,13]

The results differ greatly from those obtained by HMO calculations. All quinododimethides which can exist in only a single classical structure are predicted to be antiaromatic species. Annellation of benzenoid units to the basic structure should again greatly stabilize the system. The possible antiaromatic character of the quinododimethide portion of the structure, however, still appears to be felt. Thus, 1,2- and 1,4-naphthalene-quinododimethide (3 and 4), though they possess one benzene ring, are predicted to have only one-half the resonance energy of benzene. Only when two benze-

noid units are fused to a central nonbenzenoid quinododimethide does the resonance energy become equivalent to that of the composite parts. As a result, 9,10-anthracenequinododimethide (10) and 9,10-phenanthrenequinododimethide (14) are predicted to show a delocalization appproximately equal to twice that of benzene, while compounds 22, 24, and 25 will be equivalent to a benzene and a naphthalene unit.

The question of whether those systems for which only a single classical structure may be written (1, 2, 5, 6, 8, 21, and 31) are really antiaromatic, particularly to the large extent shown, is a moot one. The equation utilized to calculate resonance energy contains several empirical parameters. Small errors in the bond energy terms could easily produce spurious results by a cumulative effect. Dewar and de Llano, in the most recent modification of their semiempirical SCF approach, have developed a VBL technique which systematically determines the σ energy of the carbon–carbon bonds. Many of the problems associated with the use of arbitrary bond energy terms are thus avoided. Table III contains the results of such calculations on the

Table III. Results of SCF VBL Calculations[a]

System	$E_{\pi b}$	E_σ	Total E	Calcd E_{CC}	RE	REPE
1	10.646	29.175	39.821	39.726	0.095	0.012
2	10.593	29.110	39.703	39.726	−0.023	−0.004
3	17.106	47.867	64.973	63.985	0.988	0.083
4	17.074	47.843	64.917	63.985	0.932	0.078
5	16.332	47.872	64.204	63.985	0.219	0.018
6	16.263	47.720	63.988	63.985	0.003	0.000
7	23.219	66.514	89.733	88.299	1.434	0.090
8	21.982	66.623	88.605	88.299	0.306	0.019
9	23.187	66.506	89.693	88.299	1.394	0.088
10	23.572	66.578	90.150	88.299	1.851	0.116
11	23.246	66.533	89.771	88.299	1.480	0.093
12	22.812	66.526	89.338	88.299	0.961	0.063
13	23.248	66.530	89.778	88.299	1.479	0.092
14	23.572	66.588	90.160	88.299	1.861	0.116
15	23.197	66.500	89.697	88.299	1.398	0.087
16	26.272	77.837	104.109	102.568	1.541	0.086
17	26.275	77.833	104.108	102.568	1.540	0.086
18	26.287	77.862	104.149	102.568	1.581	0.088
19	26.854	77.898	104.752	102.568	2.184	0.121
20	29.137	85.190	114.327	112.500	1.827	0.091
21	27.599	85.305	112.904	112.500	0.404	0.020
22	29.688	85.231	114.919	112.500	2.419	0.130
23	29.312	85.214	114.546	112.500	2.046	0.102
24	29.380	85.244	114.624	112.500	2.124	0.106
25	29.714	85.245	114.959	112.500	2.459	0.123
26	29.530	85.194	114.724	112.500	2.224	0.111
27	29.443	85.244	114.687	112.500	2.187	0.109
28	29.213	85.226	114.439	112.500	1.939	0.097
29	29.502	85.220	114.722	112.500	2.222	0.111
30	34.976	103.982	138.958	136.758	2.200	0.092
31	33.221	104.098	137.319	136.758	0.561	0.023

[a] All energies in electron volts.

present series of quinododimethides.[14] The general trends found here qualitatively agree with the HMO results. The antiaromatic nature predicted by the SCF CBL finding for several compounds is maintained, to a greatly reduced extent, only for 1,4-benzene-quinododimethide. Quantitatively, however, the present results have marked difference with the HMO findings. The completely nonbenzenoid quinododi-

methides (**1**, **2**, **5**, **6**, **8**, **21**, and **31**), while not showing negative resonance energies, have values far less than those calculated for isomers with a partial aromatic structure and for the parent arene. The REPE for 2,3-pentacenequinododimethide is less than 20% that of pentacene itself. Concerning the possible antiaromatic nature of 1,4-benzenequinododimethide, the following is of interest. The magnetic anisotropy has been obtained for 7,7,8,8-tetraphenyl-1,4-benzenequinododimethide.[15] The experimental value is only 3.74 that of benzene despite the presence of four phenyl groups. This may be indicative of some destabilizing effect from the quinododimethide portion of the molecule.

The new approach of Dewar and de Llano definitely appears to be superior than earlier methods for determining heats of formation and related thermochemical properties such as resonance energies. This new technique, however, appears to yield values for π-binding energies which are proportional to those obtained by earlier SCF methods. Thus, a plot of the π-binding energies in Tables II and III gives a line with nearly unit slope, a correlation coefficient of unity, and very little scatter. The results of the older approaches should well describe any results whose origin lies solely in π-energy terms.

Geometries and Dipole Moments

VBL calculations show appreciable alternation of bond length in simple quinododimethides. In Table

Table IV. Some Calculated Bond Lengths[a]

Molecule	Bond	Length	Molecule	Bond	Length
1	1–2	1.464			
			14	1–2	1.396
	2–3	1.463		2–3	1.400
	3–4	1.355		3–4	1.396
	4–5	1.454		4–12	1.402
	1–7	1.355		1–11	1.402
				11–12	1.405
2	1–2	1.467		9–10	1.467
	2–3	1.351		9–14	1.468
	1–7	1.353		12–13	1.466
				9–15	1.353
4	1–2	1.468			
	2–3	1.351			
	1–9	1.468			
	5–10	1.401	**21**	1–2	1.451
	5–6	1.398		2–3	1.464
	6–7	1.398		1–13	1.378
	9–10	1.406		13–14	1.451
	1–11	1.352		5–14	1.439
				5–15	1.384
				15–18	1.444
6	1–2	1.463		6–15	1.439
	2–3	1.466		6–16	1.380
	3–4	1.352		16–17	1.441
	4–10	1.464		7–16	1.450
	1–9	1.361		7–8	1.362
	9–10	1.463		3–9	1.442
	2–11	1.355		2–19	1.360
10	1–2	1.398			
	2–3	1.398			
	1–13	1.401			
	9–13	1.469			
	13–14	1.406			
	9–15	1.352			

[a] All results in angströms.

(15) E. D. Bergman, J. Hoarau, A. Pacault, A. Pullman, and B. Pullman, *J. Chim. Phys. Physicochim. Biol.*, **49**, 474 (1952).

IV we list a few representative examples of calculated bond lengths. Relative small variation is noted among all 31 compounds. Table V lists the types of bonds

Table V. Summary of Bond Length Data[a]

Bond type	Range	Average value	Standard deviation
C=CH₂	1.352–1.361	1.354	0.001
C=C (quinonoid)	1.351–1.384	1.362	0.008
C—C (quinonoid)	1.430–1.469	1.461	0.005
C---C (benzenoid)	1.364–1.448	1.407	0.016

[a] All data in angströms.

present and information about their lengths. As can be seen, the slight variation allows for a discussion of average bond energies for single, double, and aromatic bonds. The greatest variation of bond length is associated with those bonds which would normally be regarded as aromatic. Even here, however, the range is no greater than that found in polycyclic aromatic hydrocarbons themselves. Indeed, the bond lengths of the aromatic component of a quinododimethide in most cases are nearly identical to the corresponding hydrocarbon. Thus, in compounds **10** and **14** the average aromatic bond length is 1.400 ± 0.002 Å. Compounds **22**, **24**, and **25** seem to each possess a benzene and a naphthalene moiety, compound **20** an anthracene unit, and compounds **27** and **29** phenanthrene units.

Both the CBL and VBL methods show uniform charge densities of unity on each carbon atom. This is not surprising since all the present quinododimethides are alternant hydrocarbons. A previous PPP calculation had shown a nonuniform charge distribution.[16] Earlier HMO calculations had also led to the expectation of zero dipole moments for quinododimethides.[17]

1,3-Benzenequinododimethide and Diradical Structures

The relatively high stability accorded to 1,3-benzenequinododimethide by early calculations[4,18] has been questioned in view of the hypothetical nature of the *m*-quinonoid structure. Pullman, Berthier, and Pullman explicitly showed the *m*-quinododimethide structure to be diradical in character.[19] Such systems can be regarded as Schlenk hydrocarbons.[20] Present calculations have also shown 1,3-benzenequinododimethide to be a ground state triplet. CBL calculations show a π-binding energy of 9.615 eV.[21] This is indicative of a greater degree of stability for 1,3-benzenequinododimethide than is associated with either of its two isomers, though these latter systems may assume singlet ground states. Calculations on the lowest triplets of 1,2- and 1,4-benzenequinododimethide predict that these structures should also be slightly more stable than the singlet states; the CBL values for the respective energies of these molecules are 9.064 and 9.075 eV. In view of the

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(17) A. Pullman, B. Pullman, E. D. Bergman, G. Berthier, E. Fisher, D. Ginsberg, and Y. Hirschberg, *Bull. Soc. Chim. Fr.*, **18**, 707 (1951).
(18) F. Seel, *Z. Phys. Chem., Abt. B*, **51**, 229 (1942).
(19) A. Pullman, G. Berthier, and B. Pullman, *Bull. Soc. Chim. Fr.*, **15**, 450 (1948).
(20) W. Schlenk and M. Brauns, *Chem. Ber.*, **48**, 716 (1915).
(21) Because of the slowness of convergence open shell VBL calculations were avoided.[22]
(22) J. D. Unruh and G. J. Gleicher, *J. Amer. Chem. Soc.*, **93**, 2008 (1971).

Table VI. Calculated SCF π-Binding Energy Differences between Aromatic Cyclobutenes and Quinododimethides[a]

System	CBL				VBL			
	E_{IIb}	$E_{IIb}{}^b$	ΔE_{IIb}	$\Delta\Delta E_{IIb}{}^c$	E_{IIb}	$E_{IIb}{}^b$	ΔE_{IIb}	$\Delta\Delta E_{IIb}{}^c$
1	8.910	7.825	1.085	0.000	10.646	8.752	1.894	0.000
3	14.977	13.462	1.513	0.430	17.106	14.878	2.228	0.334
5	14.165		0.703	−0.382	16.332		1.454	−0.440
7	20.585	18.924	1.661	0.526	23.219	20.809	2.410	0.516
8	19.483		0.559	−0.526	21.982		1.173	−0.721
11	20.658	19.296	1.362	0.272	23.246	21.159	2.087	0.193
12	20.176		0.880	−0.205	22.812		1.653	−0.241
13	20.663		1.367	0.282	23.248		2.089	0.195
14	21.116		1.820	0.735	23.572		2.413	0.519
18	23.524	22.336	1.188	0.103	26.287	24.355	1.932	0.038
19	24.223		1.887	0.802	26.854		2.499	0.605
20	26.024	24.332	1.710	0.625	29.137	26.640	2.497	0.603
21	24.818		0.486	−0.599	27.599		0.959	−0.935
25	26.779	25.056	1.723	0.638	29.714	27.052	2.662	0.768
26	26.468		1.468	0.327	29.530		2.478	0.584
29	26.479	25.262	1.217	0.132	29.502	27.113	2.389	0.495
30	31.461	29.718	1.743	0.658	34.976	32.412	2.564	0.670
31	30.167		0.449	−0.636	33.221		0.809	−1.085

[a] All energies in electron volts. [b] Energy of parent arene. [c] Relative to benzocyclobutene → 1,2-benzenequinododimethide.

tendency of attempted syntheses of benzenequinododimethides to yield polymeric material, the conversion of the closed-shell structure to benzylic diradical species appears logical and is in accord with these calculations.

The higher quinododimethides have also been investigated. As might be expected, those species which exist in a single localized singlet structure devoid of aromatic rings may, upon conversion to the diradical, assume a structure with appreciable benzenoid character. Compound **21** is predicted to have a triplet state 1.117 eV lower in energy than the singlet. For compound **31** the corresponding value is 1.185 eV. For higher quinododimethides which possess some aromatic character, the lowest singlet and triplet states are comparable in energy. The singlet states of 1,2- and 1,4-naphthalenequinododimethides are only ca. 0.1–0.2 eV more stable than the corresponding triplets. Only for systems such as **10** and **14** which show appreciable stabilization of the singlet state will the triplet structure be very much less stable in energy. The singlet–triplet separations for these two systems are 0.822 and 0.629 eV.

Correlation of Spectral Properties

The electronic spectra of 1,4-benzenequinododimethide, 1,4-naphthalenequinododimethide, and 9,10-anthracenequinododimethide have been obtained as films at 77°K.[23] The three compounds show absorption at 3010, 3100, and 2950 Å. The energies for these transitions correspond to 4.12, 4.01, and 4.21 eV, respectively. CBL open-shell calculations have been carried out on the first excited singlet states for these three systems.[23] Perhaps because only a single configuration was used for the excited state, the calculated energy differences for these transitions are in only fair agreement with experiment having the corresponding values of 3.38, 3.74, and 3.99 eV. The experimental data do not indicate a hypsochromic shift along the series **2**, **4**, and **10**, although such a shift is predicted by the present work and earlier HMO calculations.[17]

The results of molecular orbital calculations should also be applicable toward correlation of certain features of vibrational spectroscopy. Berthier, Pullman, and

Pontis have correlated the carbonyl stretching frequency of quinones with values of the carbonyl bond order as obtained from HMO calculations.[24] This approach should also be applicable to the exocyclic methylene group of the quinododimethides. Pearson and co-workers have obtained the solid phase ir spectra of the three compounds discussed above.[23] A detailed analysis of the spectra was not reported; however, CBL SCF calculations show a large variation in bond order and would predict measurable differences in the stretching frequencies. VBL SCF results show a smaller variation in bond order, but both approaches yield the order of energy required for compounds to undergo this vibration to be **10** > **4** > **2**.

Electrocyclic Ring Openings

The development of orbital symmetry rules by Woodward and Hoffmann has led to new interest in treating the concertedness of reactions.[25] Many ring-opening reactions are of interest, within the framework of this paper, as o-quinododimethides would be formed if a concerted process is occurring. The well-studied ring openings of derivatives of benzocyclobutene, for example, should yield substituted 1,2-benzenequinododimethides or their derivatives.[26] The effect of the fusion of other aromatic units to cyclobutene upon ring opening has been little investigated. Cava, Shirley, and Erickson have shown that naphtho[a]cyclobutene undergoes ring opening in the four-membered ring much more readily than the isomeric naphtho[b]cyclobutene,[27] a result in complete agreement with the expected greater stability of 1,2-naphthalenequinododimethide to 2,3-naphthalenequinododimethide. No other data are available. We have chosen to treat this problem by both our SCF variations. In Table VI are presented the calculated π-binding energy differences between the

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(26) R. Huisgen and H. Seidel, Tetrahedron Lett., 3381 (1964); G. Quinkert, K. Optiz, W. W. Wiersdorff, and M. Finke, ibid., 3009 (1965); K. H. Grellman, J. Palmowski, and G. Quinkert, Angew. Chem., Int. Ed. Engl., 10, 196 (1971).

(27) M. P. Cava, R. L. Shirley, and B. W. Erickson, J. Org. Chem., 27, 755 (1962).

aromatic cyclobutenes and the corresponding quinododimethides. The energies of the former compounds were assumed equal to the parent aromatics. As this approach neglects changes in the σ system and as the determination of absolute energy differences is beyond π-energy calculations, it is the relative energies which are most revealing. Not surprisingly, SCF modifications predict that those o-quinododimethides which are predicted to be least stable (**5, 8, 21,** and **31**) should not be readily formed in ring-opening reactions. For these systems any aromatic character in the cyclobutene will be lost in the quinododimethide which can maintain no benzenoid structural units. As is to be expected in cases involving only changes in π-bonding energy, the CBL and VBL methods differ slightly. Very similar results are also obtained from HMO calculations.

The data in Table VI may also be applied to the question of relative rates of ring opening if it is of course assumed that the transition state for the reaction strongly resembles the quinonoid system. The possibility of nonconcerted ring opening through a triplet diradical state can also be treated by the present approach. The relative calculated energies of quinododimethides and the corresponding triplets have already been shown to vary greatly with structure. In Table VII are presented the calculated differences in π-binding energy between aromatic cyclobutenes and the corresponding triplet diradicals as determined by the SCF CBL approach. The differences with the results in Table VI are of interest. The completely quinonoid structures associated with compounds **5, 8, 21,** and **31** are not maintained in the corresponding diradical, and these latter systems may achieve large resonance stabilization of the radical centers. Conversely, systems such

Table VII. Calculated SCF π-Binding Energy Differences between Aromatic Cyclobutene and the Corresponding Diradicals[a]

System[b]	$-E_{\Pi b}$	$-E_{\Pi b}{}^c$	$-\Delta E_{\Pi b}$	$-\Delta\Delta E_{\Pi b}{}^d$
1	9.064	7.825	1.239	0.000
3	14.708	13.462	1.246	0.007
5	14.871		1.409	0.170
7	20.344	18.924	1.420	0.181
8	20.475		1.551	0.312
11	20.529	19.296	1.333	0.094
12	20.612		1.316	0.077
13	20.503		1.207	−0.032
14	20.487		1.191	−0.048
18	23.849	22.336	1.513	0.274
19	23.531		1.195	−0.044
20	25.659	24.332	1.327	0.088
21	25.936		1.603	0.364
25	26.318	25.056	1.262	0.023
26	26.289		1.233	−0.006
29	26.390	25.262	1.128	−0.111
30	31.193	29.718	1.475	0.236
31	31.352		1.634	0.395

[a] In electron volts. [b] Systems correspond to triplet forms of quinododimethides in Figure 1. [c] Energy of parent arene. [d] Relative to benzocyclobutene → o-xylylyl diradical.

as **14** should be far more stable in closed-shell configuration and opening to a diradical will not be favored. The concertedness of ring opening in the above systems could be decided not only on the basis of stereochemical findings, but upon the relative rate of reaction. Interestingly, HMO calculations predict that all the diradical structures should be formed more readily than the o-xylylyl diradical.

J_- Acidity Scale Based on Addition of Hydroxyl Ions to Substituted Benzaldehydes[1]

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Abstract: Whereas at lower pH values benzaldehydes exist predominantly in nonhydrated form, in sodium hydroxide solutions changes in uv spectra indicate reversible addition of hydroxyl ions following reaction 6. Determination of the equilibrium constant of this reaction made it possible to evaluate the acidity function J_-. This has been found practically identical with the acidity function $J_-(k)$ obtained from kinetic data; the latter is, nevertheless, available only over a limited range of sodium hydroxide concentrations. Up to 10 M sodium hydroxide, the J_- scale also followed closely the H_- scale, but has shown deviations at higher concentrations.

Whereas a rather detailed investigation has been carried out on acidity functions for various types of acid–base systems in strongly acidic media,[3] much less attention has been paid to the scales expressing

acidity in strongly alkaline media. Two types of reactions are considered for the acid–base equilibria in aqueous alkaline solutions: hydrogen ion abstraction (1) and addition of a hydroxyl ion (2). The addition of water (or another hydroxylic solvent molecule),

$$SH + OH^- \rightleftharpoons S^- + H_2O \quad (1)$$

$$SH + OH^- \rightleftharpoons \left[S \begin{array}{c} H \\ \diagup \\ \diagdown OH \end{array} \right]^- \quad (2)$$

(1) Partly presented at the Third Northeast Regional Meeting of the American Chemical Society, Oct 11, 1971.

(2) (a) Edward Western Fellow of the Electrochemical Society, 1972; (b) Western Publishing Company Fellow of the Educational Council of the Graphic Arts, 1972–1973; (c) in partial fulfillment of the Ph.D. Thesis.

(3) C. H. Rochester, "Acidity Functions," Academic Press, New York, N. Y., 1970.