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Y VS. CYCLIC DELOCALIZATION IN SMALL RING DICATIONS AND DIANIONS: THE DOMINANCE OF CHARGE REPULSION OVER HÜCKEL AROMATICITY

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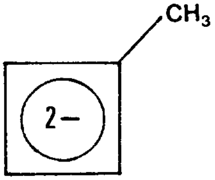
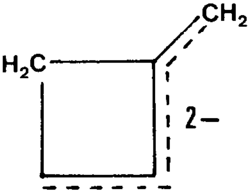
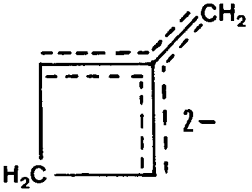
Abstract: Coulombic repulsion in four membered ring dications and dianions is more important than Hückel aromaticity and leads to a preference for Y-delocalized isomers with more favorable π charge distributions.

The most significant advances in the history of organic chemistry include the concept of cyclic aromaticity[1] and the development of Hückel π molecular orbital theory.[2] This simple one-electron treatment is remarkably successful in predicting the relative stabilities of different types of π-systems,[3] and is still used, despite the availability of more sophisticated MO methods, e.g., to evaluate the stabilisation energies of conjugated polyanions.[4] One prediction of Hückel theory which long defied experimental verification is the aromatic nature of the 6 π cyclobutadiene dianion.[5] The difficulties in obtaining this species are remarkable in view of the ease of formation of the C_4 6 π trimethylenemethane[6,7] and butadiene[8] dianions. The situation is reversed for the corresponding dications. While substituted cyclobutadiene dications are known[9] in solution (but may be non-planar and have relatively low resonance energies)[10], no trimethylenemethane dication derivatives appear to have been reported.

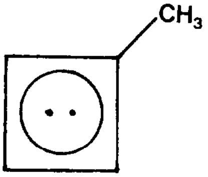
These anomalies led us to investigate small dications and dianions with MNDO SCF-molecular orbital theory.[11] All geometries were fully optimised within symmetry constraints given. Variations in π-effects are emphasised by comparing the energies of isomers with common sigma skeletons but with different delocalized π-systems: linear, Y or cyclic. The calculated heats of formation (MNDO) indicate that the Hückel stability predictions (based on β-values) do not apply to highly charged small ring systems. Y-delocalization, the advantages of which have been pointed out by Gund,[8] often is the most favorable of the three alternatives.

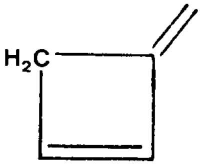


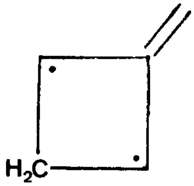




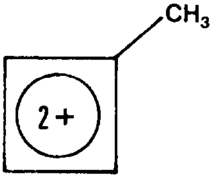
	1, C_s	2, C_s	3, C_{2v}
ΔH_f° (kcal/mol)	209.7	196.5	181.3
Resonance Energy (β)	2.000	1.618	1.732

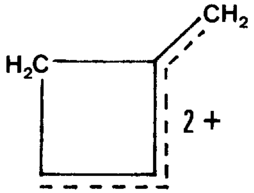


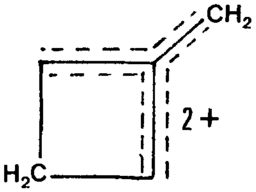




	4 C_s	5 C_s	6 C_{2v}
ΔH°_f (kcal/mol)	78.9	54.0	112.2
Resonance energy (β)	2.000	2.236	1.732



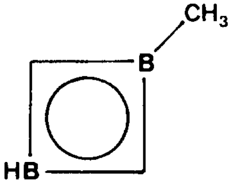


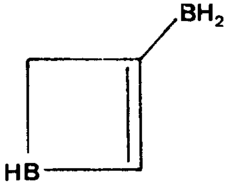


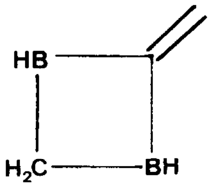
	7 C_s	8, C_s	9 C_{2v}
ΔH°_f (kcal/mol)	594.8	588.4	570.7
Resonance Energy (β)	2.000	1.618	1.732

The neutral species, 4-6, do follow the predictions of Hückel theory: the linearly conjugated system, 5, is more stable than the two antiaromatic isomers, 4 and 6. However, the doubly charged aromatic species, 1 and 7, are calculated to be the least stable forms of the three isomers considered. Even the linearly conjugated species (2 and 8), which have the lowest Hückel resonance energies in each set, are found to be more stable. The Y-delocalized dianion (3) and dication (9) are the most favorable isomers.

Coulomb repulsion, enhanced when atoms on which π charge is located are directly bonded to each other, is responsible for the relative instability of the cyclic species (1 and 7). This can be demonstrated in two ways. The neutral diboron compounds, 10-12 (the most stable isomers for their conjugation types), are isoelectronic with dications, 7-9, but are not subject to the effect of charge repulsion. Their stability order is that expected from Hückel theory: the cyclic aromatic isomer 10 is the most stable.[12]

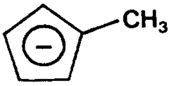


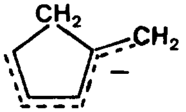




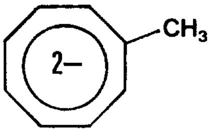
	10, C_s	11, C_s	12, C_{2v}
ΔH°_f (kcal/mol)	15.0	35.9	18.9

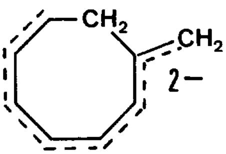
Charge repulsion is reduced in the monoanions, 13-15, as well as in the eight-membered ring dianions, 16-18, and dications, 19-21. These ions all prefer the Hückel aromatic structures:

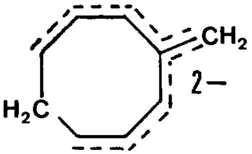




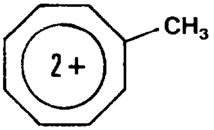
	13, C_s	14, C_s	15, C_s
ΔH_f° (kcal/mol)	5.4	24.3	35.5

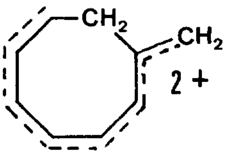


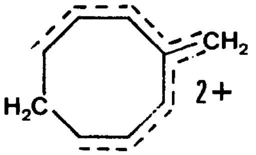




	16, C_1	17, C_1	18, C_1
ΔH_f° (kcal/mol)	112.8	130.8	142.3







	19, C_1	20, C_1	21, C_1
ΔH_f° (kcal/mol)	530.1	537.0	541.3

Small ring doubly charged ions are thus exceptional. Due to Coulombic repulsion, the cyclic Hückel aromatic forms are less favorable than their Y-delocalized counterparts, in which the π charge is largely delocalized to the peripheral atoms, or even their linearly conjugated isomers. This conclusion is supported by the observed chemistry of dianions.[4-7] Our calculations also suggest that derivatives of the trimethylenemethane dication should be easy to observe, especially as the tetramethylcyclobutadiene dication is known.[9]

Total energies of chemical species, rather than resonance energies, are of greater significance. While Hückel theory can still provide some insights and useful predictions,[1] chemists are now better served by SCF treatments which are capable of reproducing experimental energy trends.

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REFERENCES AND NOTES

(1) The literature on cyclic aromaticity is summarised by Haddon, R.C., J.Am.Chem.Soc., **1979**, 101, 1722. Also see Shawali, A.S.; Pârkânyi, C.; Herndon, W.C., J.Org.Chem., **1982**, 47, 734.

(2) Hückel, E., Z.Physik, **1931**, 70, 204. **1932**, 76, 628.

(3) Heilbronner, E.; Straub, P.A. "Hückel Molecular Orbitals". Springer Verlag, Berlin, 1966.

(4) Bates, R.B.; Hess, Jr. B.A.; Ogle, C.A.; Schaad, L.J. J.Am.Chem.Soc., **1981**, 103, 5052.

(5) The tetraphenylcyclobutadiene dianion has recently been observed, but shows extensive charge delocalization into the phenyl rings. Boche, G.; Etzrodt, H.; Marsch, M.; Thiel, W. Angew.Chem., **1982**, 94, 141; Angew.Chem.Suppl., **1982**, 345-354.

(6) Klein, J.; Medlik, A. J.C.S.Chem.Comm., **1973**, 275.

(7) Bates, R.B.; Beavers, W.A.; Greene, M.G.; Klein, J.H. J.Am.Chem.Soc., **1974**, 96, 5640; Bahl, J.J.; Bates, R.B.; Beavers, W.A.; Mills, N.W. J.Org.Chem., **1976**, 41, 1620.

(8) Gund, P. J.Chem.Ed., **1972**, 49, 100. Also see Phelan, N.F.; Orchin, M. J.Chem.Ed., **1968**, 45, 633.

(9) Olah, G.A.; Staral, J.S. J.Am.Chem.Soc., **1976**, 98, 6290.

(10) Krogh-Jespersen, K.; Schleyer, P.v.R.; Pople, J.A.; Cremer, D. J.Am.Chem.Soc., **1978**, 100, 4301; Chandrasekhar, J.; Krogh-Jespersen, K.; Schleyer, P.v.R. J.Comput.Chem., **1981**, 2, 356.

(11) Dewar, M.J.S.; Thiel, W. J.Am.Chem.Soc., **1977**, 99, 4899, 4907; **4** and **6** were calculated as open shell singlets using the half-electron method. The eight membered rings adopt either flattened boat or chair conformations.

(12) The corresponding diaza compounds, which are isoelectronic with the dianions **1**-**3**, prefer non-planar nitrogens which complicate comparison with fully conjugated π-systems.

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