Symmetry Requirements for the Stabilization of One Class of Diradicals

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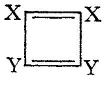
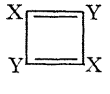
A TRIPLET ground state can exist for a molecule whenever there are only two electrons to be placed in a pair of degenerate or nearly degenerate orbitals. Such degeneracy may occur for both molecules which have normal Kekulé structures (*e.g.* cyclobutadiene[1]) and for formal diradicals (*e.g.* trimethylenemethane). The stability of the lowest singlet state may be increased by breaking as seriously as possible the degeneracy of the nonbonding orbitals. Where geometry allows it, a very effective procedure for accomplishing this is the distortion from maximum molecular symmetry to a less symmetrical structure. This is probably what occurs in the ground state of cyclobutadiene.[2] Symmetry breaking may also be accomplished by replacing carbon by hetero-atoms, or by substitution or annelation by groups with low-lying unoccupied molecular orbitals (good acceptors in the normal terminology) or high-lying occupied molecular orbitals (good donors).[3]

Indiscriminate replacement or substitution may often result in simultaneous lowering or raising of *both* components of the degenerate pair, with no net stabilization of the singlet. For maximum symmetry-breaking effect one should perform the replacement or substitution so as to destabilize or stabilize only one level of the degenerate pair, or, better, to destabilize one and stabilize the other. The symmetry arguments for devising the best strategy are described below for cyclobutadiene.

Consider a cyclobutadiene substituted by two groups X with low-lying unoccupied π^* orbitals and two groups Y with high-lying occupied π levels. There are two possible substitution patterns, (1) and (2). The degenerate orbital pair of a square cyclobutadiene may be chosen in two ways,[4] appropriate to the ensuing loss of symmetry on formation of (1) or (2).

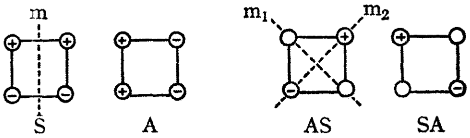


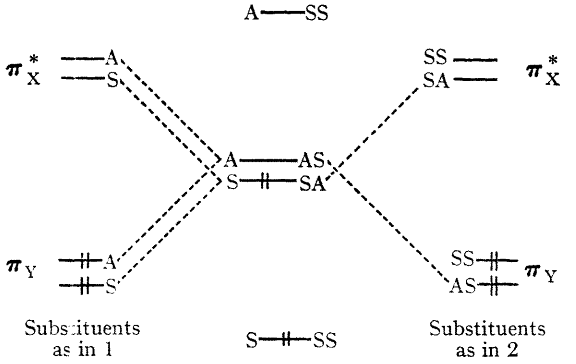
(1)



(2)

The interaction diagrams below show the very different features of (1) and (2). In (1), X and Y each provide a level of correct symmetry to interact with *either* level of the degenerate cyclobutadiene pair. The net splitting is unpredictable. In (2), X provides a level of the correct symmetry to *depress* one level of the degenerate pair, and Y provides a level of just the requisite symmetry to *raise* the other.† It is now easy to understand why despite the extensive work directed toward the synthesis of "push–pull" cyclobutadienes[5] the goal was achieved only recently with a compound of type (2).[6]





Similarly, replacement of two or four carbon atoms of the cyclobutadiene by hetero-atoms will produce a superior symmetry-breaking of the degenerate level pair if the replacement is as in (4) rather than as in (3). In (3) both originally nonbonding molecular orbitals S and A are affected by the presence of W and Z. In (4), one molecular orbital, say SA, is entirely composed of W orbitals, whereas the other, AS, is entirely made up of Z. If there is a sizable difference in electronegativity between W and Z, then (4) exploits that difference fully. To support the symmetry argument two cases were studied in an extended Hückel calculation. For the dimers of HCN, where W = CH and Z = N the splitting is 0·66 ev for (3) and 2·39 ev for (4). For the case W = BH, Z = NH the corresponding symmetry-breaking amounts to 2·86 ev for (3) and 5·89 ev for (4).[7]

(3)

(4)

The simple symmetry arguments presented here are not restricted to cyclobutadiene. They are easily extended to cases such as cyclo-octatetraene, where once again alternate substitution or replacement [similar to (2) or (4)] would lead to stabilization of the planar geometry.[8] The symmetry arguments are applicable to a still wider class of substituted hydrocarbons, and a particularly intriguing application which we will shortly describe is the design of molecules which are singlet ground states but by proper substitution can be transformed into triplet ground states.

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† Hückel calculations for the case of two substituents have been reported (H. E. Simmons and A. G. Anastassiou, in M. P. Cava and M. J. Mitchell, eds., "Cyclobutadiene", Academic Press, New York, 1967, p. 394). They substantiate the symmetry analsyis, as do unpublished CNDO calculations by M. Gheorghiu in this laboratory. A conventional count of ionic valence bond structures also favours (2), but we find the molecular orbital analysis more illuminating.

[1] For other examples of this type see C. F. Wilcox, jun., *Tetrahedron Letters*, 1968, 795.

[2] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, 1965, **87**, 3255; L. C. Snyder, *J. Phys. Chem.*, 1962, **66**, 2299; *J. Chem. Phys.*, 1960, **33**, 619 and references therein.

[3] See, *e.g.* the suggestion by J. D. Roberts, *Chem. Soc. Special Publ. No.* 12, 1958, 111, amplified in S. L. Mannatt and J. D. Roberts, *J. Org. Chem.*, 1959, **24**, 1336, on "push-pull" methylenes. See also ref. 5, and our own work on stabilizing singlet methylenes and nitrenes: R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 1475; R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *ibid.*, p. 1485; R. Gleiter and R. Hoffmann, *ibid.*, p. 5457; *Tetrahedron*, 1968, **24**, 5899.

[4] See, *e.g.*, J. D. Roberts, "Notes on Molecular Orbital Calculations" Benjamin, New York, 1962, p. 75. S and A indicate respectively symmetry or antisymmetry with respect to the indicated mirror planes *m*.

[5] R. Breslow, D. Kivelevich, M. J. Mitchell, W. Fabian, and K. Wendel, *J. Amer. Chem. Soc.*, 1965, **87**, 5132.

[6] R. Gompper and G. Seybold, *Angew. Chem.*, 1968, **80**, 804 (X = CO_2Et, Y = NEt_2).

[7] Here a derivative has been known for some time: M. F. Lappert and M. J. Majumdar, *Proc. Chem. Soc.*, 1963, 88; "Boron–Nitrogen Chemistry" Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D.C., 1964, p. 208.

[8] A BN analogue of cyclo-octatetraene, however, exists in the "tub" geometry: H. S. Turner and R. J. Warne, *Proc. Chem. Soc.*, 1962, 69; "Boron–Nitrogen Chemistry", Advances in Chemistry Series, No. 42, Amer. Chem. Soc., Washington, D.C., 1964, p. 290.