Scheme I
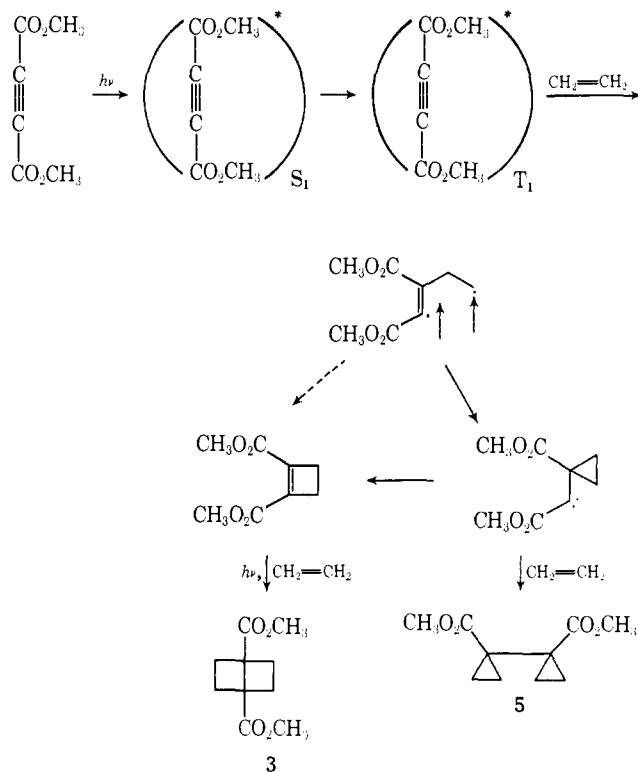

vestigating the photoaddition of other unsaturated substrates to dimethyl acetylenedicarboxylate.

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Walsh's Rules as the Rule of the Closed Shell[1,2]

Sir:

Consider a molecule M, of formula AH_mB_n, comprising m hydrogen atoms H and n other first-row atoms B, bound to a central heavy atom A, in a linear or nonlinear configuration if $m + n = 2$, in a planar or nonplanar configuration if $m + n = 3$, and so on. Cases for which ligands are bound to one another are excluded. Then it has been well known since the work of Walsh in 1953[3] that the stable configuration of M can be predicted from the number of valence electrons of M. Namely, molecules HAH are linear if they have 4 or fewer valence electrons, molecules HAB are linear if they have 10 or fewer valence electrons, molecules CAB are linear if they have 16 or fewer valence electrons, molecules AH_3 are planar with 6 or fewer valence electrons, molecules BAH_2 are planar with 12 or fewer valence electrons, molecules BACH are planar with 18 or fewer valence electrons, and molecules BACD are planar with 24 or fewer valence electrons. A lower symmetry occurs when the number of valence electrons exceeds the number indicated. For

HAB and CAB, linearity results again for 16 or more and 22 or more valence electrons, respectively.

The Walsh rules as just stated refer to most ground states of stable species; Walsh's own discussion included excited states. The rules were viewed by Walsh, and they have been viewed by most subsequent authors, as being a consequence of molecular orbital theory, although their elucidation from molecular orbital theory is not yet complete.[4] We here initiate a discussion more reminiscent of valence bond theory.

Noting that Walsh's magic numbers can all be recovered from the formula

$$W = 2m + 8n \tag{1}$$

we see that Walsh's rules are equivalent to the following prescription. Assign valence electrons to the ligand hydrogen atoms until each possesses a closed shell of two electrons, and assign valence electrons to the ligand heavy atoms until each possesses a closed octet. If there are no (or a negative number of) valence electrons left over, the molecule takes its most symmetric configuration; if there are valence electrons left over, the molecule assumes a lower symmetry.[5]

The closed-shell configurations here invoked may be viewed as ionic valence bond structures; for example, $H^-Be^{2+}H^-$ for BeH_2 (linear), $H^-O^{2+}H^-$ for H_2O (nonlinear), $H^-C^{4+}N^{3-}$ for HCN (linear), $H^-C^{3+}O^{2-}$ for HCO (nonlinear), $N^{3-}N^{5+}O^{2-}$ for N_2O (linear), $O^{2-}N^{4+}O^{2-}$ for NO_2 (nonlinear), and $N^{3+}H_3^{3-}$ for NH_3 (nonplanar). This very ionicity provides a mechanism for holding the molecule in its most symmetric configuration or causing its distortion, depending on the absence or presence of excess valence electrons on the central atom. Coulomb repulsion between ligand ions preserves the high symmetry unless a counter force of comparable magnitude arises. That can happen through 2s–2p hybridization at the central atom when excess electrons are there, producing finite atomic dipoles in the field of which the ligand atoms are displaced toward positions of lower symmetry. Degeneracy between 2s and 2p orbitals on the central cation would make this effect formally a second-order Jahn–Teller effect.[6] The atomic dipoles could then be created with no loss in energy and the distortion would occur with a gain in stability. In the foregoing examples, the electronic configurations of the central ions are Be^{2+} $(1s)^2$, O^{2+} $(1s)^2(2s$ or $2p)^4$, C^{4+} $(1s)^2$, C^{3+} $(1s)^2(2s$ or $2p)$, N^{5+} $(1s)^2$, N^{4+} $(1s)^2(2s$ or $2p)$, and N^{3+} $(1s)^2(2s$ or $2p)^2$; the possibility for such distortions being favorable is clear in the second, fourth, sixth, and seventh cases.

The reference closed-shell ionic structure must have the same symmetry as the molecular state of interest, and the appropriate reference ionic structures may not always permit the formation of an asymmetric hybrid. Symmetries of actual low-lying molecular states require that the p_σ orbitals on the central ion be the last to be

(3) A. D. Walsh, *J. Chem. Soc.*, 2260, 2266, 2296, 2301 (1953).
(4) Among the key more recent discussions are the following: W. A. Bingel, *J. Chem. Phys.*, 30, 1250, 1254 (1959); 32, 1522 (1960); Z. *Naturforsch. A*, 16, 668 (1961); C. E. Wulfman, *J. Chem. Phys.*, 31, 381 (1959); 33, 1567 (1960); C. A. Coulson and A. H. Nielson, *Discuss. Faraday Soc.*, 35, 71 (1963); S. E. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, 45, 734 (1966).
(5) This prescription may also be found in R. D. Gillard, *Rev. Port. Quim.*, 11, 70 (1969).
(6) Compare R. G. Pearson, *J. Chem. Phys.*, 52, 2167 (1970); *J. Amer. Chem. Soc.*, 91, 4947 (1969); R. F. W. Bader, *Can. J. Chem.*, 40, 1164 (1962).

Table I. Bond Angles of Triatomic Molecules[a]

Molecule[b]	Bond angle Exptl[c]	Calcd[d]	Molecule[b]	Bond angle Exptl[c]	Calcd[d]
BH_2	131	118	$SO_2(^3B_1)$	126	140
$CH_2(^1A_1)$	102	100	ClO_2	118	122
$CH_2(^3B_1)$		120	NO_2	134	144
$CH_2(^1B_1)$		119	O_3	117	128
NH_2	103	101	ONF	110	119
$NH_2(^2A_1)$	144	120	HCF	111	101
H_2O	105	102	$HCF(^1A'')$	127	120
NF_2	104	105	HCO	120	131
OF_2	104	107	HNO	109	113
AlH_2	119	117	$HNO(^1A'')$	116	132
PH_2	92	99	HPO	105	110
$PH_2(^2B_1)$	123	118	$HCCl$	103	101
H_2S	92	99	$HSiCl$	103	99
SiF_2	101	99	$HSiCl(^3A'')$	116	118
SO_2	120	120	SSO	118	122

[a] Species predicted to be linear include the $^2B_1$(II) state of BH_2 and the ground states of HCN, CO_2, BO_2, C_3, N_3, CNO, CNS, CCN, CNC, and XeF_2. [b] Ground states unless otherwise indicated. [c] From Table 62 of ref 8, except that the bond angle for OF_2 is taken from L. E. Sutton, Ed., Chem. Soc., Spec. Publ., No 11, M67 (1958). [d] Calculated from a point-charge model of closed-shell ionic structures, as described in the text.

occupied. Thus HAB molecules revert to linearity with 16 or more electrons because the configuration $(1s)^2(2s)^2(2p_\pi)^4$ cannot become asymmetric. CAB molecules revert to linearity with 22 or more electrons for the same reason. Effects of electronic excitation on shape are accounted for nicely—the governing feature is the number of electrons which can occupy asymmetric hybrids. The reference structure for one state of NH_2 has the configuration $(1s)^2(2s–2p$ hybrid$)^2(2p_\pi)$ on the nitrogen atom, while another reference structure has the configuration $(1s)^2(2s–2p$ hybrid$)(2p_\pi)^2$. The former is a $^2B_1$ state, the latter $^2A_1$; the bond angle is smaller in the former because it has two electrons in the dipole-producing hybrid. Similarly, the lowest triplet state $^3B_1$ for CH_2 should be bent. There should be two low singlet states for CH_2, one $^1B_1$ with a bond angle near that of the triplet and one $^1A_1$ with smaller bond angle.[7] On the other hand, the planarity of CH_3[8] remains an exception in the present approach, as it does in the simple molecular orbital pictures.[9]

By including d orbitals, Hayes modified Walsh's molecular orbital diagrams to account for the non-linearity of certain alkaline earth dihalides.[10] A similar modification can be made in the present approach by invoking formation of asymmetric pd hybrids on the central alkaline earth ions.

To test these ideas, we have calculated equilibrium bond angles for a number of molecules by minimizing the total electrostatic energy for the simplest conceivable model for the closed-shell ionic structures: integral point charges at ligand atoms, integral point charges at the centers of charge of central-ion digonal sp hybrids built from Slater orbitals, and bond distances their equilibrium values. Results are given in Table I.

The magnitudes of the angles are roughly right and trends from molecule to molecule are reproduced amazingly well. We have also computed bending force constants for this model. Their orders of magnitude are correct—some high and some low, by factors usually <2.

In summary, there is a straightforward and simple reformulation of Walsh's rules as a rule of the closed shell, and a corresponding model which is useful for predicting bond angles. If bond distances were very large in the closed-shell ionic structure for one of these molecules, and if the 2s and 2p orbitals on the central ion were strictly degenerate, there is no doubt that the molecule would distort or not for the reasons we have given. But why the method works for actual molecules is a mystery.

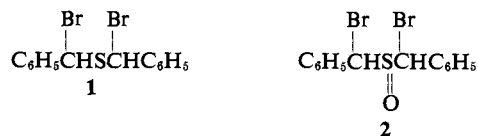Yuuzi Takahata, Gary W. Schnuelle,[11] Robert G. Parr*
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2,3-Diphenylthiirene 1-Oxide

Sir:

We wish to describe the synthesis of 2,3-diphenylthiirene 1-oxide (2,3-diphenylvinylene sulfoxide) (3), the first member of a new series of 3-heterocyclopropenes which is doubly unique in being both potentially aromatic, assuming the possibility of d orbital conjugation effects,[1] and potentially antiaromatic,[2] in view of the presence of an unshared electron pair on the heteroatom. The sulfoxide 3 was synthesized by bromination of dibenzyl sulfide to give in 37% yield the sensitive but isolable dibromide 1:[3] mp 78–81.5°;

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   Br Br                        Br Br
   |  |                         |  |
C6H5CHSCHC6H5              C6H5CHSCHC6H5
     1                          ‖
                                O
                                2
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nmr ($CDCl_3$) δ 6.47 (s, CH), 7.35 (m, phenyl). Oxidation of 1 by means of perbenzoic or m-chloroperbenzoic acid generally gave (76%) only one of the stereoisomeric dibromosulfoxides 2, namely the racemic isomer:[4] mp 121–123.5°; ir ($CHCl_3$) 9.32 μ (S–O); nmr ($CDCl_3$) δ 5.53 (s, 1, CH), 6.26 (s, 1, CH), 7.45

(1) (a) L. A. Carpino and L. V. McAdams, III, J. Amer. Chem. Soc. 87, 5804 (1965); (b) L. A. Carpino and R. H. Rynbrandt, ibid., 88, 5682 (1966); (c) L. A. Carpino, L. V. McAdams, III, R. H. Rynbrandt, and J. W. Spiewak, ibid., 93, 476 (1971); (d) M. E. Volpin, Y. D. Koreshkov, V. G. Dulova, and D. N. Kursanov, Tetrahedron, 18, 107 (1962).
(2) For a consideration of possible antiaromaticity effects in 3-heterocyclopropenes see (a) D. T. Clark, Proc. Israel Acad. Sci. Humanities, 238 (1970); (b) D. T. Clark, Theor. Chim. Acta, 15, 225 (1969). We are indebted to Professor Clark for preprints in advance of publication.
(3) This compound could not be sufficiently purified for elemental analysis. All other new compounds gave correct elemental analyses (±0.3%) and consistent spectral data.
(4) The racemic structure is assigned on the basis of the observed magnetic nonequivalence of the methine protons. In addition oxidation of 2 by means of m-chloroperbenzoic acid gave in 76% yield only racemic α,α'-dibromodibenzyl sulfone: mp 161.5–162.5°; nmr ($CDCl_3$) δ 6.30 (s, 1, CH), 7.47 (m, 5, phenyl). This is in agreement with the recent assignment by Bordwell and coworkers of the isomer, mp 157–159°, as the meso isomer by X-ray crystallography [F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, J. Amer. Chem. Soc., 90, 5298 (1968)]. See also C. Y. Meyers and A. M. Malte, ibid., 91, 2123 (1969).

(7) For recent discussions of this species, see C. F. Bender and H. F. Schaefer III, J. Amer. Chem. Soc., 92, 4984 (1970); R. A. Bernheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, J. Chem. Phys., 53, 1280 (1970); J. F. Harrison and L. C. Allen, J. Amer. Chem. Soc., 91, 807 (1969).
(8) G. Herzberg, "Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1966, p 609.
(9) See, for example, p 2298 of ref 3.
(10) E. F. Hayes, J. Phys. Chem., 70, 3740 (1966).