Table I. Bond Angles of Triatomic Molecules[a]

Molecule[b]	Bond angle Exptl[c]	Bond angle Calcd[d]	Molecule[b]	Bond angle Exptl[c]	Bond angle 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 $^2B_1(\Pi)$ 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 $(1s)^2(2s\text{-}2p\text{ hybrid})^2(2p_\pi)$ on the nitrogen atom, while another reference structure has the configuration $(1s)^2(2s\text{-}2p\text{ hybrid})(2p_\pi)^2$. 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 nonlinearity 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.

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(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).

(11) National Science Foundation Trainee.

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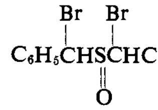
2,3-Diphenylthiirene 1-Oxide

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°;


$C_6H_5\overset{\text{Br}}{\overset{|}{C}}HS\overset{\text{Br}}{\overset{|}{C}}HC_6H_5$

1


$C_6H_5\overset{\text{Br}}{\overset{|}{C}}H\underset{\text{O}}{\underset{\|}{S}}\overset{\text{Br}}{\overset{|}{C}}HC_6H_5$

2

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

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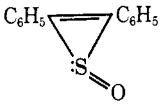
(1) (a) L. A. Carpino and L. V. McAdams, III, *J. Amer. Chem. Soc.* **87**, 5804 (1965); (b) L. A. Carpino and R. H. Rynbrandt, *ibid.*, **88**, 5682 (1966); (c) L. A. Carpino, L. V. McAdams, III, R. H. Rynbrandt, and J. W. Spiewak, *ibid.*, **93**, 476 (1971); (d) M. E. Volpin, Y. D. Koreshkov, V. G. 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).

(m, 10, phenyl). Treatment of **2** with 20 mol equiv of triethylamine in refluxing methylene dichloride for 3 days gave in 50% yield the sulfoxide **3**: mp 92.5–93.1°; ir ($CHCl_3$) 9.42 μ (S–O); nmr ($CDCl_3$) δ 7.52 (m, 6, *m*- and *p*-phenyl), 7.87 (m, 4, *o*-phenyl); uv (95% C_2H_5OH) nm (log ϵ) 220 (4.41), 227.5 (4.40), 292.5 sh (4.40), 299 (4.45), 310 sh (4.38).



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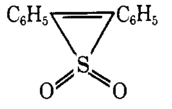


4

The unusual structure **3** is assigned on the basis of its oxidation by means of *m*-chloroperbenzoic acid (refluxing for 20 hr in methylene dichloride) to the corresponding sulfone **4** (25% yield), the structure of which has been firmly established in previous work.[1a,c] In view of the fact that conjugative effects of sulfones generally appear to be greater[5] than those of sulfoxides it is surprising that sulfoxide **3** is markedly more stable than sulfone **4**. For example a solution of **3** in refluxing benzene showed only slight decomposition after 24 hr whereas similar treatment of **4** results in complete decomposition after less than 6 hr. Although **4** decomposes at its melting point, **3** is stable at 130° for 10 min and is only partially destroyed after 1 hr.[6–8] In addition, in its spectral properties sulfoxide **3** shows greater resemblence to the carbocyclic model, diphenylcyclopropenone (**5**), than does sulfone **4**.[1a,c]

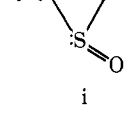
Thus the ultraviolet spectrum of **3** is closely similar to that of the ketone **5** whereas **4** shows a spectrum which, while generally similar, resembles even more closely an "insulated" analog such as 1,2-diphenylcyclopropene-3-carboxylic acid. Similarly the nmr spectrum of **3** suggests greater conjugative effects than are apparent in the case of **4**. Analogously to **5**, sulfoxide **3** exhibits two distinct areas of complex absorption presumably associated with the (a) ortho and (b) meta and para proton multiplets centered at δ 7.87 and 7.52,[10] respectively, whereas **4** shows only a single, less complex multiplet at δ 7.55.[14] These preliminary observations suggest a fundamental difference between the S–O bond of a rigid cyclic sulfoxide and that of a corresponding sulfone. It is also clear from the properties described that the presence of an unshared pair of electrons on the heteroatom leads to no special instability in the case of **3**.[16] Whether antiaromaticity is important in the case of other 3-heterocyclopropenes remains to be seen. Lack of success[19] in previous attempts to synthesize such compounds has sometimes been attributed to this factor. However in none of these cases, with the possible exception of the thiirenes,[19c,e,f] has there been the possibility of electron-attracting conjugative stabilization involving the heteroatom.

In view of the greater and more varied reactivity of sulfoxides relative to sulfones, **3** promises to be a more useful intermediate than **4** for interconversions in the 3-thiacyclopropene series. Reactions such as deoxygenation and conversion to ylides and sulfonium salts, etc., are currently under investigation.

Acknowledgment. This study was generously supported by grants (NSF GP-4283 and GP-10152) from the National Science Foundation.

(5) (a) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968); (b) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709 (1963); (c) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, pp 138–139.

(6) Conceivably, the lesser thermal stability of the sulfone could simply reflect the more facile extrusion of SO_2 relative to SO. In line with this effect it has been possible to isolate both *cis*- and *trans*-i (C. H. Han, unpublished). Both isomers are significantly more stable toward thermal decomposition than the corresponding sulfones the trans isomer[7] of which has not yet been isolated in a pure state. Quantitative comparisons are now required.



i

(7) F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *J. Amer. Chem. Soc.*, 90, 429 (1968).

(8) Diphenylcyclopropenone has a half-life of about 5 min at 190°.[9]

(9) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, 87, 1320 (1965).

(10) At least part of the separation between the ortho, meta, and para protons must be due to the anisotropic effects of one phenyl group on the ortho protons of the other.[11] For example, methyl 1,2-diphenylcyclopropene-3-carboxylate[12] shows a similar although less pronounced separation into two multiplets at δ 7.60 and 7.40. For 1,2-diphenylcyclopropene the aromatic multiplet is reported to appear between 7.0 and 7.9 ppm.[13] In addition specific effects of the S–O group may be involved.

(11) S. Andreades, *J. Amer. Chem. Soc.*, **87**, 3941 (1965).

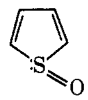
(12) R. Breslow, R. Winter, and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

(13) D. T. Longone and D. M. Stehouwer, *Tetrahedron Lett.*, 1017 (1970).

(14) In view of the complexity of the spectra it has not yet been possible to obtain unequivocally the position of the para proton in the case of **3** and **4**. Since conjugative effects would be best related to this absorption,[11,15] deuterio-substituted derivatives of **3**, **4**, and **5** are under study.

(15) Compare (a) D. G. Farnum, *J. Amer. Chem. Soc.*, **86**, 934 (1964); (b) D. G. Farnum and C. F. Wilcox, *ibid.*, **89**, 5379 (1967); (c) D. G. Farnum, *ibid.*, **89**, 2970 (1967); (d) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); (e) A. R. Katritzky and R. D. Topsom, *Angew. Chem., Int. Ed. Engl.*, **9**, 87 (1970).

(16) It is interesting in this connection that thiophene 1-oxide (ii)[17] and 1,1-dioxide (iii)[18] are both relatively unstable in comparison with thiophene.



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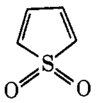

iii

(17) M. Prochazka, *Collect. Czech. Chem. Commun.*, **30**, 1158 (1965).

(18) W. J. Bailey and E. W. Cummins, *J. Amer. Chem. Soc.*, 76, 1932, 1936 (1954).

(19) (a) F. W. Fowler and A. Hassner, *ibid.*, **90**, 2875 (1968); (b) J. Meinwald and D. H. Aue, *ibid.*, **88**, 2849 (1966); (c) R. Zahradnik, *Advan. Heterocycl. Chem.*, **5**, 14 (1965); (d) D. J. Anderson, T. L. Gilchrist, and C. W. Rees, *Chem. Commun.*, 147 (1969); (e) I. G. Csizmadia, J. Font, and O. P. Strausz, *J. Amer. Chem. Soc.*, **90**, 7360 (1968); (f) O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *ibid.*, **89**, 4805 (1967); (g) R. N. McDonald and P. A. Schwab, *ibid.*, **86**, 4866 (1964); (h) J. K. Stille and D. D. Whitehurst, *ibid.*, **86**, 4871 (1964).

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