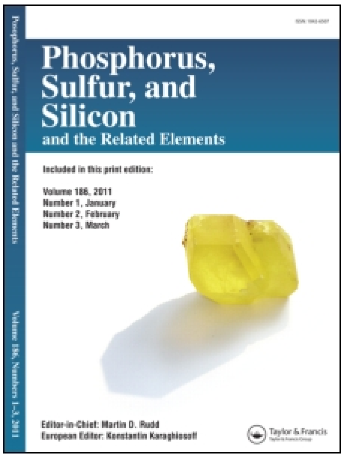
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Thiocumulenes (S-Centered 1,3-Dipoles)-a Theoretical View

JÜRgen Fabian

To cite this Article Fabian, JÜRgen(1999) 'Thiocumulenes (S-Centered 1,3-Dipoles)-a Theoretical View', Phosphorus, Sulfur, and Silicon and the Related Elements, 153: 1, 357 — 358

To link to this Article: DOI: 10.1080/10426509908546469

URL: http://dx.doi.org/10.1080/10426509908546469

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur and Silicon, 1999, Vol. 153-154, pp. 357-358
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

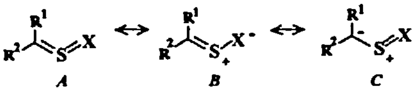
Thiocumulenes (S-Centered 1,3-Dipoles)- a Theoretical View

JÜRGEN FABIAN

Institut für Organische Chemie der Technische Universität Dresden, Germany
D-01062 Dresden, Mommsenstraße 13

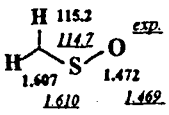
Structure and reactions parameters of sulfines were calculated by DFT at the B3LYP/6-311+G(3df) and by *ab initio* methods at the G2(MP2) level of theory. The particular features of the sulfines are discussed.

Compounds are traditionally called sulfur-centered heterocumulenes (**1**) when sulfur is twice doubly-bonded to adjacent carbon atoms or heteroatoms. According to Huisgen et al. these compounds are 1,3-dipoles.[1] Sulfines (thiocarbonyl *S*-oxides, **1d**) are better known than other compounds of series **1**.[2,3] Because of their unique structural features and their high reactivity compounds such as **1a**[4], **1b**[5] and **1c**[6] have been recently studied theoretically. This study *mainly deals with sulfines. The sulfines were calculated by non-parametric quantum chemical* methods (DFT and *ab initio* methods) using the GAUSSIAN-94 codes of programs. Some more recent theoretical studies on sulfines are quoted in Ref. 7.



1a $X=CR_2$, **1b** $X=NR$, **1c** $X=S$, **1d** $X=O$

The geometries of sulfines are very well reproduced by DFT calculations (cf. Figure 1, for the parent compound). The charges calculated by natural population analysis[8] correspond to formula *B*. This conclusion is supported by the weights of the charge-separated Lewis-type structures calculated by the natural resonance theory of Glendening and Weinhold.[8] The weight of the hypervalent structure *A* is remarkably high though the population of the d-orbitals is low. There is an additional long-bond (singlet biradical) Lewis-type structure structure (*D*) that one generally encounters in NRT analyses of 1,3-dipolar structures.



NPA charges (π-charges)
C: -0.71 (-0.14)
O: +1.52 (+0.82)
S: -0.90 (-0.68)
μ = 3.12 debye (*exp. 2.99*)

NRT weighting
A: 17.1%
B: 46.0%
C: 13.9%
D: 7.9%

FIGURE 1 Molecular and electronic structure of the parent sulfine (Exp. cf. Ref. 3)

The functional groups of the sulfines of thiopropionaldehyde, thioadamantanone, 2,2,4,4-tetramethyl-3-thioxocyclobutanone, thiotropone and thiofluorenone are closely related structurally to sulfine except for thiotropone with a marked CS bond lengthening (in good agreement with the X-ray structure[7c]).

Two types of pericyclic reactions are considered in Figure 2. Since the molecular geometries and reaction energies are sensitive to f-functions DFT B3LYP calculations were performed with the basis set 6-311+G(3df). The results of *ab initio* G2(MP2) calculations are reported for comparison. The results of the DFT and *ab initio* calculations are similar (cf. Figure 2). The ring closure reaction of the parent sulfine is endothermic in contrast to the corresponding reactions of **1a** - **1c** (R^1, R^2 = H) while the activation energy is larger. The prototype sulfine-to-ethene cycloaddition reaction is less exothermic than the correponding reactions of **1a** to **1c** (R^1, R^2 = H). The results of the calculations reflect the particular position of **1c** in series **1**.

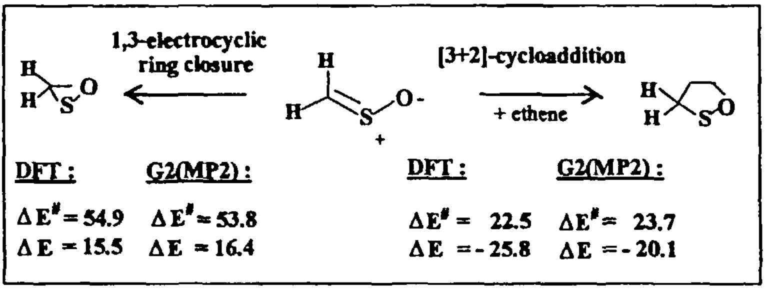


FIGURE 2 Reaction parameters of pericyclic reactions of the parent sulfine in kcal/mol (without zero point vibrational energies)

Since [2+4]-cycloaddition reactions of sulfines are encountered more frequently than 1,3-dipolar cycloadditions both the [3+2]-cycloaddition and [2+4]-cycloaddition of the parent sulfines to cyclopentadiene were calculated. The DFT activation barrier of the [2+4]- is lower by about 10 kcal/mol than the barrier of the [3+2]-cycloaddition. The reverse holds for the reactions of the parent thioformaldehyde *S*-methylide (**1a**, R^1, R^2 = H).

References

[1] R. Huisgen, G. Mloston and K. Polborn *J. Org. Chem.* 61, 6570 (1996).

[2] B. Zwanenburg *Phosphorus, Sulfur Silicon Relat. Elem.* 43, 1 (1989).

[3] E. Block, *Angew. Chem.* 104, 1159 (1992), and earlier papers quoted therein.

[4] J. Fabian and B. A. Hess Jr., *J. Org. Chem.* 62, 1766 (1997).

[5] J. Fabian and G. Mloston, to be published; G. Mloston and J. Fabian, to be published.

[6] J. Fabian and A. Senning, *Sulfur Reports* 21, 1 (1998).

[7] (a) A. Klesing and D.H. Sutter, *J. Mol. Struct.* 352/353, 357 (1995); (b) D.J. Clouthier, J.M. Vollmer, *ibid.* 354, 49 (1995);(c) P.J.A. Ruttink, P.C. Burgers, J.T. Francis, J. K. Terlouw, *J. Phys, Chem.* 100, 9694 (1996); (c) T. Machiguchi, T. Hasegawa, M. Otani, S. Yamabe and H. Mizuno, *J. Amer. Chem. Soc.* 116, 407 (1994); (d) R. Huisgen, G. Mloston, K. Polborn, R Sustmann and W. Sicking, *Liebigs Ann./Recl.* 1997, 179.

[8] E.D. Glendening and F. Weinhold, *J. Comput. Chem.* 195, 593 (1998).