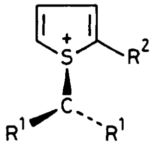
A ^1H N.M.R. and *Ab initio* SCF-MO Study of Thiophenium Methylides

Timothy Bowles,[a] Alexander E. A. Porter,[a]* Josef A. Rechka,[a] and Henry S. Rzepa[b]*

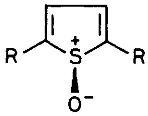
[a] *Chemistry Department, University of Stirling, Stirling FK9 4LA, Scotland, U.K.*
[b] *Chemistry Department, Imperial College, London SW7 2AY, U.K.*

A ^1H dynamic n.m.r. and *ab initio* SCF-MO study of thiophenium methylides (**1**) indicates that the compounds have lower inversion barriers at sulphur than the corresponding aliphatic ylides; the unusual stability of (**1**) may arise from conjugation of the sulphur lone pair with the ring.

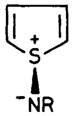
Thiophenium methylides[1] (**1**) display certain unexpected properties. Although the sulphur atom is highly pyramidal[1] with the substituents attached to the ylide carbon orthogonal to the thiophene ring [*cf.* Figure 1(b)], the ^1H and ^{13}C n.m.r. chemical shifts and general stability are comparable to those of thiophene itself,[2] suggesting a significant degree of aromaticity. The chemical reactivity of compounds (**1**) is also considerably lower than might be expected on the basis of the reactions of the isoelectronic sulphoxides[3] (**2**) and sulphilimines[4] (**3**), which tend to display characteristics of antiaromatic systems. In view of these properties, we felt it important to measure the barrier to inversion at sulphur in (**1**), particularly since in aliphatic sulphur ylides[5] and sulphoxides[6] such barriers are relatively high and stereoisomers can be resolved at room temperature due to chirality at sulphur. We report here a ^1H n.m.r. and *ab initio* SCF-MO model study of (**1**) which suggests that the inversion barrier at sulphur in these systems is lower than in aliphatic ylides and which offers a possible explanation for the differing behaviour of (**1**) and (**2**).



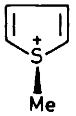
(1)



(2)



(3)



(4)

The derivative (**1**, $R^1 = CO_2Bu^t$, $R^2 = CH_2Ph$)† contains a prochiral benzyl group which is an exclusive ^1H n.m.r. probe for inversion at sulphur, and the non-equivalent ester groups which may serve as a ^1H n.m.r. probe for either inversion at sulphur or rotation about the ylidic carbon–sulphur bond. Lineshape analysis[7] at 250 MHz of the benzylic AB spin

---

† All new compounds exhibited satisfactory spectroscopic properties, elemental analyses, and/or accurate mass data.

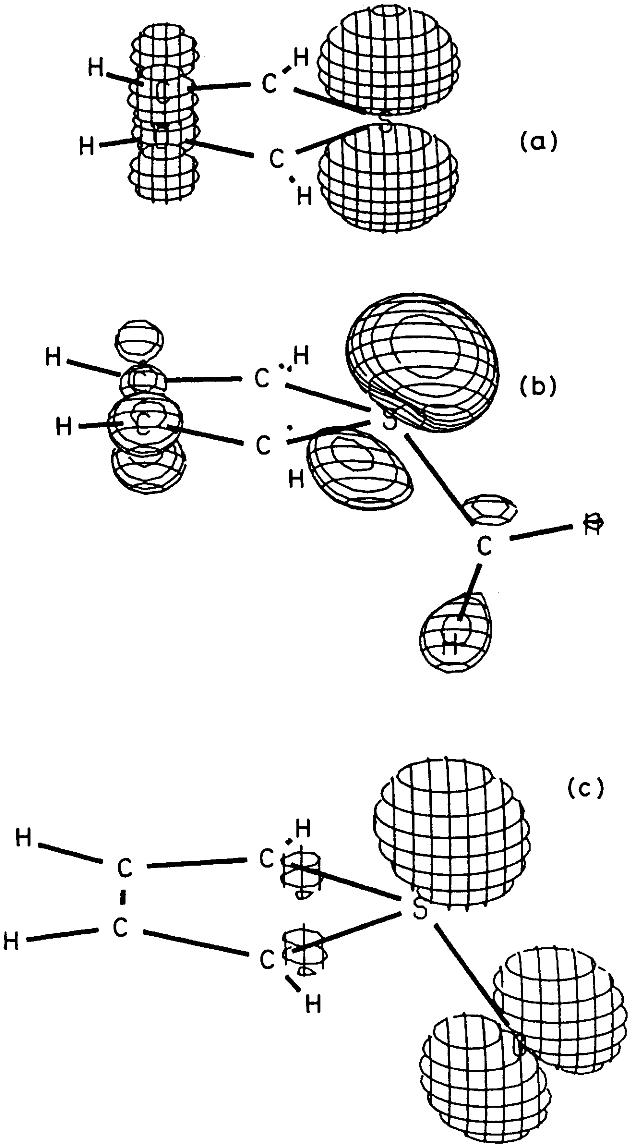


Figure 1. The wavefunction corresponding to (a) the highest occupied MO of thiophene, (b) the HOMO−1 of ($\mathbf{1}$, $R^1 = R^2 = H$), and (c) the HOMO of ($\mathbf{2}$).

system‡ resulted in the activation parameters $\Delta H^{\ddagger}$ 70.6 ± 1.2, $\Delta G^{\ddagger}{}_{298}$ 51.7 ± 1.1 kJ mol^{-1}, and $\Delta S^{\ddagger}$ 63.5 ± 0.3 J mol^{-1} K^{-1}. A study of the dimethyl ester gave similar but less accurate results owing to some overlap of resonances ($\Delta H^{\ddagger}$ 73.6 ± 5.9, $\Delta G^{\ddagger}{}_{298}$ 52.3 ± 5.6 kJ mol^{-1}, and $\Delta S^{\ddagger}$ 71.3 ± 1.5 J mol^{-1} K^{-1}). The values of $\Delta G^{\ddagger}$ are smaller than that measured for the sulphoxide ($\mathbf{2}$, R = Me[CH$_2$]$_4$CMe$_2$–) by Mock[3] and preclude the possibility of isolating diastereoisomers due to chirality at sulphur. The value of $\Delta S^{\ddagger}$ for an inversion process is normally close to zero,[8] whereas our values are surprisingly high. This may reflect the extra degree of rotational freedom which is introduced about the carbon–sulphur bond in the transition state.

Table 1. Calculated *ab initio* properties of ($\mathbf{1}$, $R^1 = R^2 = H$) and ($\mathbf{4}$).

	(1)	(4)
$E_{\text{tot}}{}^{a,b}$/a.u. Ground state^c	−587.2848 (−583.5707)	−587.7294 (−584.1166)
$r_{\text{C-S}}{}^c$/pm	160.4	181.4
$E_{\text{rel}}{}^d$ Transition state^e	55 (70)	137 (146)
$r_{\text{C-S}}{}^c$/pm	157.8	179.8
$E_{\text{rel}}{}^d$ Transition state^f	113 (111)	
$r_{\text{C-S}}{}^c$/pm	170.0	
$E_{\text{rel}}{}^d$ Transition state^g	113 (110)	

[a] 1 a.u. = 2626 kJ mol^{-1}. [b] Obtained using a STO 3-21G* basis set,[9] with the STO 3G* values shown in parentheses. [c] Molecular geometries were initially optimised using the MNDO SCF-MO method (M. J. S. Dewar and M. L. McKee, *J. Comp. Chem.*, 1983, **4**, 84, and refs. cited therein) and with the exception of variables associated with the ring hydrogens, geometries were reoptimised at the STO 3G* basis set level.[9] The STO 3-21G* calculations were carried out at the 3G* optimised geometries (3-21G*//3G*). [d] Energy relative to the ground state, in kJ mol^{-1}. [e] Transition state for sulphur inversion. [f] Transition state for carbon–sulphur rotation with the carbon lone pair *cis* to the thiophene ring. [g] Transition state for carbon–sulphur rotation with the carbon lone pair *trans* to the thiophene ring.

The rate constants derived from lineshape analysis of the t-butyl ester groups in ($\mathbf{1}$, $R^1 = CO_2Bu^t$, $R^2 = CH_2Ph$) are consistently higher at lower temperatures than those derived from the prochiral benzyl group, leading to the activation parameters $\Delta^{\ddagger}H$ 56.1 ± 2.2, $\Delta G^{\ddagger}{}_{298}$ 53.3 ± 2.0 kJ mol^{-1}, and $\Delta S^{\ddagger}$ 9.3 ± 0.6 J mol^{-1} K^{-1}. Although individual values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from such kinetic analyses are known to be prone to large systematic errors,[8] it is possible that the present results indicate that the spin exchange observed for the two ester groups is not purely due to inversion about sulphur but contains a contribution from rotation about the ylide carbon–sulphur bond. In this case the interpretation of the activation parameters is not simple, but the lower $\Delta S^{\ddagger}$ value is consistent with a significant participation of the rotation process.

In order to estimate the relative energy of sulphur inversion and carbon–sulphur bond rotation, we carried out *ab initio* restricted Hartree–Fock calculations[9] on the parent ylide ($\mathbf{1}$, $R^1 = R^2 = H$) and the protonated form ($\mathbf{4}$). These serve as models representing the two limits of delocalisation of the formal negative charge on the ylidic carbon atom. The results (Table 1) at the STO 3-21G*//3G* level show the calculated inversion barrier ($\Delta H^{\ddagger}$ 55 kJ mol^{-1}) in ($\mathbf{1}$) to be significantly smaller than the rotation barrier ($\Delta H^{\ddagger}$ 113 kJ mol^{-1}) and in reasonable agreement with our experimental results. The high rotational barrier is a consequence of significant p_{π}–d_{π} bonding between the ylidic carbon and the sulphur atom. For ($\mathbf{4}$), little such bonding is possible and the rotational barrier may be assumed to be small, whereas the inversion barrier at sulphur is calculated to increase to $\Delta H^{\ddagger}$ 137 kJ mol^{-1}. Clearly there is a stage of delocalisation of the carbanionic centre in which the rotational and inversion barriers become equal. Our ^{1}H n.m.r. results with ($\mathbf{1}$, $R^1 = CO_2Bu^t$, $R^2 = CH_2Ph$) indicate that this molecule may indeed be close to this point. By introducing suitable electron-withdrawing groups on the ylidic carbon or manipulating the steric effects with *ortho* substituents, it should be possible to control the relative heights of the rotational and inversion barriers, and this work is currently in progress.

---

‡ Spectra were recorded as 1% w/v solutions in CD$_2$Cl$_2$. The temperature dependence of δ_{AB} was monitored in the pre-exchange region and extrapolated where necessary. The temperatures were calibrated using a standard methanol sample.

Inspection of the canonical molecular orbital [Figure 1(b)] corresponding to the lone pair on sulphur in (**1**, $R^1 = R^2 = H$) shows significant conjugation with the ring π system and similarity with the equivalent π orbital in thiophene itself [Figure 1(a)].[10] In contrast, the closest equivalent molecular orbital in (**2**) is not significantly conjugated with the thiophene ring system [Figure 1(c)]. This may explain the widely differing properties of (**1**) and (**2**) and suggests that (**2**) should have properties more closely related to a diene than to the aromatic thiophene.

Received, 2nd March 1984; Com. 277

References

1 R. J. Gillespie, J. Murray-Rust, P. Murray-Rust, and A. E. A. Porter, *J. Chem. Soc., Chem. Commun.*, 1978, 83.

2 A. E. A. Porter in 'The Chemistry of Thiophenes,' vol. I, ed. S. Gronowitz, Wiley, New York, in the press.

3 W. L. Mock, *J. Am. Chem. Soc.*, 1970, **92**, 7610.

4 O. Meth-Cohn and G. van Vuuren, *J. Chem. Soc., Chem. Commun.*, 1984, 190.

5 D. Darwish and R. L. Tomlinson, *J. Am. Chem. Soc.*, 1968, **90**, 5938.

6 D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, 1966, **88**, 3138.

7 D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, 1968, **90**, 4854; using the program DNMR3H, W. Stempfle, J. Klein, and E. G. Hoffman, Quantum Chemistry Program Exchange, 1977, **11**, 450, and the Cyber 180/855 Computer at Imperial College Computer Centre.

8 G. Binsch and H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 411.

9 Using the Gaussian 76 program system, J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, Quantum Chemistry Program Exchange, 1978, **11**, 368, on the CRAY-1S/1000 computer at the University of London Computer Centre and the Imperial College Cyber 180/855 computer. The STO 3-21G* basis sets were obtained from W. J. Pietro, M. M. Franc, W. J. Hehre, D. J. DeFrees, J. A. Pople, and J. S. Binkley, *J. Am. Chem. Soc.*, 1982, **104**, 5039, and references cited therein.

10 Using the program PSI/77, W. L. Jorgensen, Quantum Chemistry Program Exchange, 1977, **11**, 340.