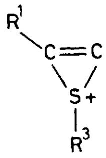
Low Temperature *X*-Ray Molecular Structure of 1-Methyl-2-3-di-t-butylthiirenium Tetrafluoroborate, the First Example of Stable Thiirenium Salts

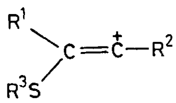
By RICCARDO DESTRO, TULLIO PILATI, and MASSIMO SIMONETTA*
(*Istituto di Chimica Fisica e Centro C.N.R., Università, Via Golgi* 19, 20133 *Milano, Italy*)

Summary The geometry at 173 K of the thiirenium ion, a new heterocyclic unsaturated three-membered system, is described; the cation shows a pyramidal conformation.

EVIDENCE has been presented[1] that thiirenium ions (**1**) are involved as reactive intermediates in both the addition of sulphenyl halides to acetylenes and in unimolecular substitution reactions of β-thiovinyl sulphonates. Non-empirical SCF–MO calculations have been performed[2] on the $C_2H_2SH^+$ cation, with optimization of four limiting structures corresponding to pyramidal and planar thiirenium ions (**1**) and to *s-cis-* and *s-trans*-vinyl cations (**2**). It was found that the pyramidal bridged structure was somewhat more stable than both open structures, whereas the planar bridged structure was on an energy maximum. Indeed, some thiirenium ions have been detected[3] by n.m.r. spectroscopy as stable species in liquid SO_2 at low temperature.[4] The synthesis and isolation of stable thiirenium salts, recently reported,[5] allowed us to perform a diffractometric investigation for the full characterisation of this heterocyclic system.



(1)



(2)

Crystal data (at 173 K): $[C_{11}H_{21}S]^+[BF_4]^-$, *M* 272·2, monoclinic, space group $P2/c$, $a = 13{\cdot}711(2)$, $b = 8{\cdot}473(1)$, $c = 13{\cdot}397(2)$ Å, $\beta = 113{\cdot}79(2)°$; $D_c = 1{\cdot}269$ g cm^{-3}, $Z =$

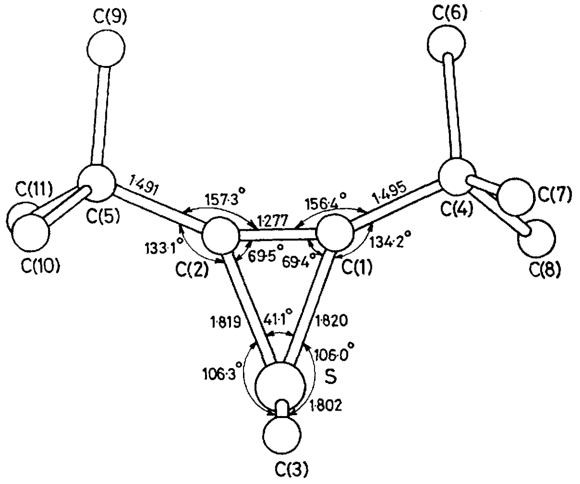


FIGURE. The structure of the thiirenium ion viewed in a direction perpendicular to the three-membered ring; only some of the relevant bond distances and angles involving heavy atoms are shown. E.s.d.'s are in the range 0·002—0·003 Å in bond lengths and 0·05—0·20° in bond angles.

4, μ(Mo-K_α) = 2·51 cm^{-1}. 3454 intensities were measured on a computer-controlled four-circle diffractometer, using graphite-monochromatized Mo-K_α radiation. The structure was solved by standard Patterson and Fourier techniques. Least-squares refinement based on 3329 reflexions with $I > 0$ gave an R of 0·055 (non-H atoms anisotropic, H atoms isotropic).†

The essential features of the geometry of the bridged cation are shown in the Figure. The prediction[2] of a pyramidal conformation is confirmed; however, the calculated value of the angle between the S–C(3) bond and the bisector of the C(1)–S–C(2) angle differs by *ca.* 10° from the experimental value (97·96 *vs.* 107·4°). The length of S–C(3) bond compares favourably with that for a C(sp^3)–S bond, as found in dimethyl sulphide (1·803 Å).[6] The ring S–C bond lengths are consistent with the expected absence of any double bond character; an excessive lengthening for such bonds (up to 2·051 Å) resulted from quantum mechanical calculations.[2] The C(1)–C(2) distance can be compared with that of the C=C bond in cyclopropene [1·29(4) Å (electron diffraction)].[7] Atoms C(3), C(4), and C(5) are displaced from the plane of the three-membered ring by −1·721(2), 0·023(2), and −0·041(2) Å, respectively.

There are two crystallographically distinct BF_4^- anions, each lying on a twofold axis; one of them is disordered. Difficulties were encountered in attempting to interpret the 'banana'-shaped electron densities obtained in the Fourier maps for the F atoms of the latter anion. Several models were investigated; the final adopted model consists of two separate tetrahedral rigid groups with a B–F distance of 1·38 Å. There are only negligible changes (*ca.* 0·01 Å) in the cation geometry with different models for the BF_4^- disordered anion. The ordered BF_4^- group is held tightly by pairs of cations, each of them contributing with an S ··· F contact of 3·034 Å, significantly less than the sum of van der Waals radii.

We thank Professor G. Modena for a sample of the crystals and Dr R. Bianchi for computing assistance.

(*Received*, 9*th May* 1977; *Com.* 443.)

---

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, 1971, **9**, 185; P. S. Stang, *Progr. Phys. Org. Chem.*, 1973, **10**, 276; G. Modena, G. Scorrano, and U. Tonellato, *J.C.S. Perkin II*, 1973, 493, and references cited therein.

[2] I. G. Csizmadia, A. J. Duke, V. Lucchini, and G. Modena, *J.C.S. Perkin II*, 1974, 1808; I. G. Csizmadia, F. Bernardi, V. Lucchini, and G. Modena, *ibid.*, 1977, in the press.

[3] G. Capozzi, O. De Lucchi, V. Lucchini, and G. Modena, *J.C.S. Chem. Comm.*, 1975, 248.

[4] Spectroscopic evidence for the occurrence of a stable long-lived vinyl cation in the reaction of a vinyl halide with antimony pentafluoride has also been reported: H. U. Siel, J. C. Carnahan, jr., L. Eckes, and M. Hanack, *Angew. Chem. Internat. Edn.*, 1974, **13**, 675.

[5] G. Capozzi, V. Lucchini, G. Modena, and P. Scrimin, *Tetrahedron Letters*, 1977, 911.

[6] W. Maier, *Angew. Chem.*, 1961, **73**, 120.

[7] J. D. Dunitz, H. G. Feldman, and V. Schomaker, *J. Chem. Phys.*, 1952, **20**, 1708.