Stabilization of the Tris(2-Thienyl)methyl Cation by Formation of Polymethine Units. A Thiophene S–S Intramolecular Interaction

Teresa Varea,[a] **Mercedes Medio-Simón,**[a] **Belén Abarca,**[a] **Rafael Ballesteros,**[a] **Gregorio Asensio,***[a] **Santiago García-Granda,**[b] **Enrique Pérez-Carreño**[b] **and Fermín Gómez-Beltrán**[b]

[a] *Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, 46100-Burjassot (Valencia), Spain*

[b] *Departamento de Química Fisica y Analitica, Facultad de Quimica, Universidad de Oviedo, 33006-Oviedo, Spain*

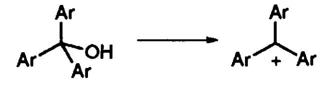
The tris(2-thienyl)methyl cation **2a**$^+$ is stabilized by delocalization over a conjugated polymethine framework; it shows restricted rotation about the C–S bond induced by S–S interaction and crystallizes as a statistically disordered racemic mixture of two enantiomeric species.

The stabilization of carbenium ions by thiophene units[1] has led to their use as the end groups in new redox systems such as tetrathienylethylenes which are readily converted in dications by electrochemical oxidation.[2] Absence of the interactions between *ortho* hydrogen atoms as observed in the propeller-shaped arylcarbenium ions[3,4] makes it possible for dithienylcarbenium units to adopt a nearly planar arrangement, allowing the effective delocalization of positive charge over a polymethine subunit.[2] These findings prompted us to study the crystal structure of the tris(2-thienyl)methyl cation to be compared with those of the above mentioned mono- and di-cations.

The carbinol **1a**[1] was converted into the perchlorate **2a**$^+$ ClO_4^- by a procedure similar to that for the synthesis of **2b**$^+$.[3] It was dissolved in acetic anhydride and the resulting solution poured on to 60% aqueous perchloric acid giving rise to a solution of **2a**$^+ClO_4^-$ which was stored at room temperature to give brown crystals that were used for the X-ray structure analysis.† The crystal structure of **2a**$^+ClO_4^-$ (Fig. 1) showed the presence in the solid state of two thiophene rings (A, B) with the sulfur atoms facing each other and a third non-equivalent statistically disordered thiophene ring (C).

By contrast conformational analysis according to the rigid-rotor approximation in the MMX program‡ reveals the global minimum conformation of ion **2a**$^+$ to be propeller-shaped with adjacent thiophene rings at angles of 35°. The three sulfur atoms lie on a plane parallel to that defined by the three coplanar central bonds, each facing the corresponding H(3) atom of the adjacent ring (Fig. 2). The calculated global minimum conformation for **2a**$^+$ (symmetry *C* correlates well with the X-ray structure reported for triphenylmethyl perchlorate (**2b**$^+ClO_4^-$) which is propeller-shaped with adjacent aromatic rings at angles of 54° (symmetry *D*).[3]§ The X-ray structure of **2a**$^+$ now reported differs from that of the calculated global minimum conformation since one of the thiophene rings (A) is twisted by 180°. The averaged angles between heteroaromatic rings are 47°. The molecule is asymmetric in such a way that two enantiomeric conformations are defined, and compound **2a**$^+ClO_4^-$ crystallizes as a racemic mixture.

In the structure of **2a**$^+$, bond lengths and angles in two of the thiophene rings (A, B) show that they are similar while the third (C) is different (see Fig. 1). Bond lengths and angles in rings A and B follow the same trend as in the dithienylcarbenium moiety in tetrathienylethylene dications,[2] while ring C is markedly distorted, owing partly to the presence of



1 **2**$^+$

a; Ar = 2-Thienyl
b; Ar = Ph

Scheme 1

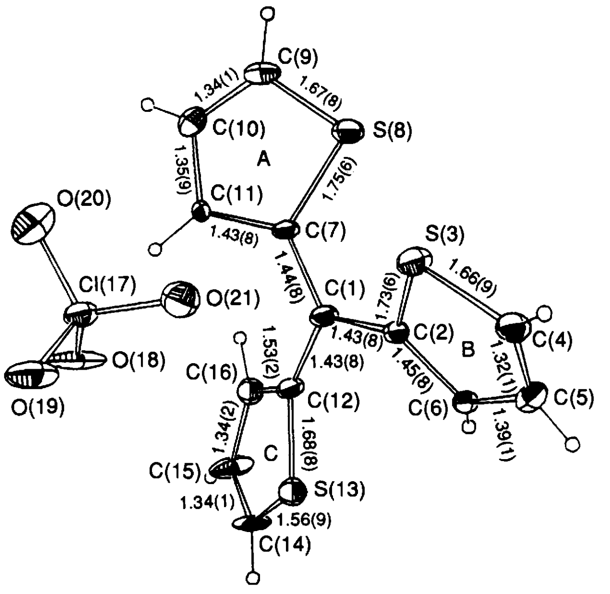


Fig. 1 ORTEP drawing of the crystal structure of cation **2a**$^+$. Alternative positions for disordered atoms have been removed for simplicity. Bond lengths are given in Å.

---

† *Crystal Data*, **2a**$^+ClO_4^-$ triclinic, space group $P\bar{1}$ (No. 2), M_r = 360.85, a = 8.491(8), b = 9.625(3), c = 9.918(2) Å, α = 116.90(3), β = 90.41(2), γ = 94.79(2)°, V = 719.4(4) Å^3, Z = 2, D_c = 1.67 Mg m^{-3}. Mo-Kα radiation (graphite crystal monochromator, λ = 0.71073 Å), μ(Mo-Kα) = 6.92 cm^{-1}, F(000) = 368, T = 293 K. ω–2θ scan technique ($0 < \theta < 25°$). Final conventional R-factor = 0.054 (R_w = 0.055) for 1319 observed reflections [$I > 3\sigma(I)$] and 219 variables. The structure was solved by direct methods (SHELX86[8]) and Fourier synthesis. Lorentz and polarisation corrections were applied. Anisotropic refinement for non-hydrogen atoms, except for the disordered C(13) and S(16).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ MMX program package from Serena Software Ltd, Bloomington, IN. The MMX molecular mechanics program was established from the MM2 and MMP1 programs (Allinger QCPE 395 and QCPE 318) by K. E. Gilbert and J. J. Gajeswski. Although the MMX program has been reported as a suitable method for calculations with benzenoid polycyclic aromatic hydrocarbons (B. F. Plummer, S. J. Rusell and G. W. Reese, *J. Org. Chem.*, 1991, **56**, 3219) the presence of sulfur atoms in the cation **2a**$^+$ can decrease this suitability. Nevertheless, the results obtained are useful qualitatively. For **2a**$^+$, minimization was performed using the bond length values obtained from the X-ray analysis while standard values from the program were used for bond angles.

§ The MMX molecular mechanics calculation predicts for cation **2b**$^+$ a global minimum for the propeller-shaped structure with angles of 46° between adjacent aromatic rings.

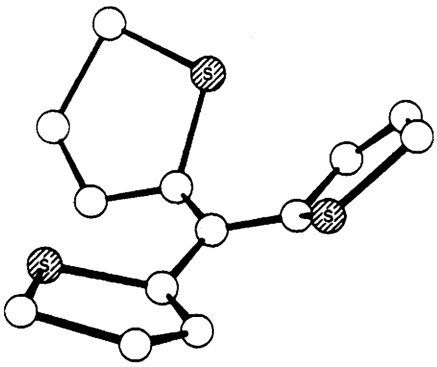


Fig. 2 Global-minimum energy conformation found for cation **2a**$^+$ by molecular mechanics calculations

disorder. A strain energy calculation, according to the rigid-rotor approximation in the MMX program for the conformation found for **2a**$^+$ in the X-ray structure, shows this to be +7.7 kcal mol^{-1} (1 cal = 4.184 J) relative to the calculated global minimum conformation.‡ The explanation for the non-equivalence of the three thiophene rings and the adoption by **2a**$^+$ of a conformation in the crystal different from that corresponding to the calculated global minimum may be attributed to the presence of a polymethine unit with 12 electrons distributed over 11 atoms and also to the existence of an intramolecular non-bonded S–S interaction.[5] It is to be noted that the distance between the facing sulfur atoms in the rings A and B is as low as 3.206(3) Å, *i.e.* 0.4 Å shorter than the sum of the van der Waals radii of sulfur.[6]

The charge distribution must fit a different pattern for rings A and B or C. In fact, Parthasarathy[7] has shown that the majority of S–S interactions in crystals may be regarded as the incipient formation of an attractive electrophile–nucleophile pairing. This view would couple rings A and B with the positive charge delocalized over the polymethine unit[2] and the interacting terminal sulfur atoms. By contrast, the charge in ring C would follow the classical π-delocalization pattern.

The stabilization of **2a**$^+$ *via* a polymethine unit and the existence of an S–S 'non-bonded contact' could explain the fact that ion **2a**$^+$ does not prefer, in the solid state, the conformation corresponding to the global minimum which is calculated without considering these stabilizing forces, and also the presence of two enantiomeric species in the crystal, as a suitable model for the statistical disorder found. This type of behaviour appears to be general for dithienyl carbenium ions as the structure of monocation **2a**$^+$ is similar to that found by Miyashi *et al.*[2] for 5-thiomethyl substituted dications derived from tetrathienylethylene.

This research was supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT Project PB90-0412). T. V. acknowledges the Spanish Ministerio de Educación y Ciencia for a predoctoral fellowship.

Received, 9th March 1993; Com. 3/01376F

References

1 B. Abarca, G. Asensio, R. Ballesteros and C. Luna, *Tetrahedron Lett.*, 1986, 5657; B. Abarca, G. Asensio, R. Ballesteros and T. Varea, *J. Org. Chem.*, 1991, **56**, 3224.

2 T. Suzuki, H. Shiohara, M. Monobe, T. Sakimura, S. Tanaka, Y. Yamashita and T. Miyashi, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 455.

3 A. H. Gomes de Mesquita, G. H. MacGillavry and K. Eriks, *Acta Crystallogr.*, 1965, **18**, 437.

4 N. C. Baenziger, R. E. Buckles and T. D. Simpson, *J. Am. Chem. Soc.*, 1967, **89**, 3405.

5 F. Wudl, G. Srdanov, B. Rosenau, d. Wellman, K. Williams and S. D. Cox, *J. Am. Chem. Soc.*, 1988, **110**, 1316; A. E. Koziol, R. C. Palenik and G. J. Palenik, *J. Chem. Soc., Chem. Commun.*, 1988, 226; R. Bensassi, U. Folli, D. Iarossi, L. Schenetti, F. Taddei, A. Musatti and M. Nardelli, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1989, 1741, and references cited therein.

6 L. Pauling, *The Nature of the Chemical Bond,* 3rd edn., Cornell University Press, Ithaca, New York, 1960; pp. 260. New data for the radius of sulfur, reported by S. C. Nyburg and C. H. Faerman, *Acta Crystallogr., Sect. B*, 1985, **41**, 274, are in agreement with the existence of a sulfur–sulfur interaction.

7 T. N. Guru Row and R. Parthasarathy, *J. Am. Chem. Soc.*, 1981, **103**, 477.

8 G. M. Sheldrick C. Krüger and R. Goddard, SHELX86, in *Crystallographic Computing 3,* Clarendon Press, Oxford, 1985, p. 175.