Tetrahedron Letters, Vol. 34, No. 5, pp. 847-850, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

The First Diazatetrathiafulvalenes

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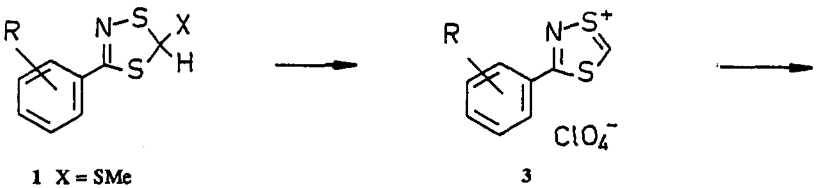
Abstract: **Treatment of 1,4,2-dithiazolium salts, unsubstituted at C-5, with triethylamine yields mixed geometrical isomers of 5-(1,4,2-dithiazol-5-ylidene)-1,4,2-dithiazoles, in 10-28% yields; *X*-ray analysis of the *trans*-3,3'-diphenyl derivative 5a shows the molecules to be planar and to stack along the *b* direction with close perpendicular intra-stack distances of 3.56 Å.**

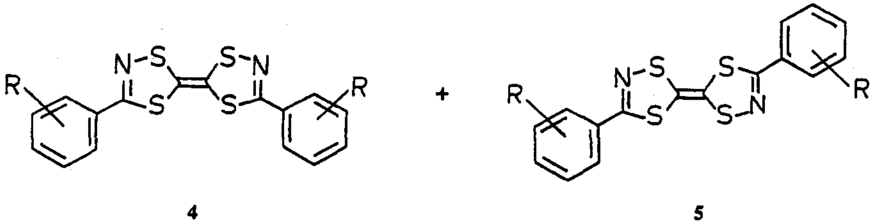
Tetrathiafulvalenes and their selena- and tellura-analogues have been the subject of extensive studies in the search for organic conductors and superconductors, and the field has been well reviewed.[1] The recent preparation of bis(ethylenedioxy)tetrathiafulvalene[2] and a superconducting derivative[3] has demonstrated the advantages of incorporating a small electronegative atom, both electronically, and in terms of enhanced intermolecular interactions. To date, no examples have been reported of tetrathiafulvalenes in which a carbon atom in the five-membered rings has been replaced by nitrogen. We were interested in the effect such a structural change would have on the properties of these interesting molecules, and now report the first examples of diazatetrathiafulvalenes, the 5-(1,4,2-dithiazol-5-ylidene)-1,4,2-dithiazoles **4** and **5**.

1,3-Dithiolium salts unsubstituted at C-2 are readily converted into tetrathiafulvalenes.[4] In a similar fashion, although less readily, the 1,4,2-dithiazolium salts **3**, prepared from the dithiazoles **1**[5,6] or **2**[6] by solvolysis with 70% $HClO_4$ in acetic anhydride, yield, on treatment with 2 mol equiv. of Et_3N in acetonitrile at 0°C, mixed geometrical isomers of the red diazatetrathiafulvalenes **4** and **5** (10-28%). The (major) *trans*-



1 X = SMe
2 X = N[CH$_2$]$_5$

3

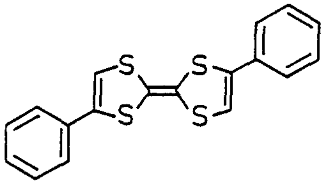


4

5

a; R = H, **b**; R = 4-Cl, **c**; R = 3-Cl,
d; R = 4-Br, **e**; R = 4-OMe, **f**; R = 3-OMe

isomers **5** may be separated from the more-soluble *cis*-compounds **4** by recrystallisation ($CHCl_3$ or $CHCl_3$/hexane), and obtained pure for spectroscopic characterisation.[7] The UV spectrum (cyclohexane) of **5a** [410 nm (ε_{max} 4 770 $dm^3\ mol^{-1}\ cm^{-1}$), 319 (24 500), 284 (56 700) and 260 (32 800)] was remarkably similar to that for the tetrathiafulvalene analogue **6** [412 (6 300), 328 (22 200), 280 (27 400) and 260 (30 700)].



6

X-Ray analysis[8] of **5a** (Fig 1) confirms the *trans*-configuration. In sharp contrast with the close analogue **6**,[10] and some other tetrathiafulvalenes,[2a,11] the atoms of the fulvalene ring system are all coplanar, with, in this case, the two phenyl rings also lying in the same plane. The largest deviation from the mean plane as defined by all non-hydrogen atoms is 0.017 Å for C(1). Thus, substitution of CH by N causes significant changes in geometry,[12] leading to a flattening of the five-membered ring, and also bringing about a shortening of the C(1)-C(1') bond [1.353(14)Å in **6**; 1.332(2)Å in **5a**].

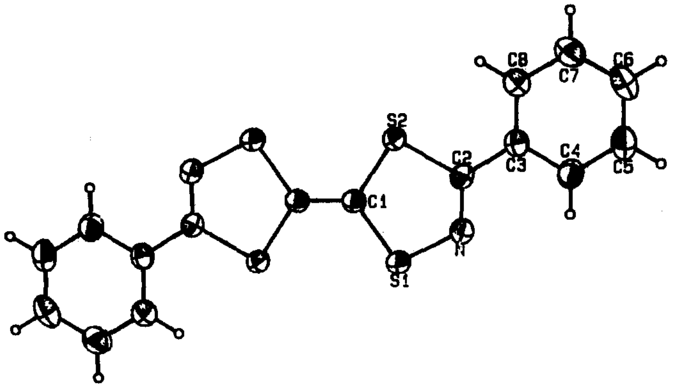


Fig. 1. Ortep drawing of the molecule. Thermal ellipsoids are drawn at 50% probability level

Of particular interest, however, is the mode of packing. Looking down the *b* axis (Fig. 2), pairs of molecules are related by a centre of symmetry, but are not coplanar, giving rise to intermolecular S(1)...S(2) distances which range from 3.713 to 3.832 Å. This is apparent in the stereoscopic view along the *a* axis (Fig. 3), in which it can also be seen that the molecules are stacked parallel to, and above one another in columns along the *b* direction, giving a close perpendicular intra-stack distance of 3.56 Å. There is potential for decreasing the observed inter- and intra-stack distances, and thus increasing S...S interactions, by formation of suitable salts. The cyclic voltammogram of **5a** [Glassy carbon electrode versus SCE; electrolyte $Bu_4N^+PF_6^-$ (0.1 M) in CH_2Cl_2, scan rate 50 mV s^{-1}] showed two single electron oxidations with peak values of 0.65 and 0.98 V respectively, which are a little larger than those for compound **6**.[13] The first was reversible, while the second only became so at an increased scan rate of 500 mV s^{-1} when the corresponding half wave potentials were 0.72 and 1.07 V. This showed the cation radical to be relatively stable, but the dication to be susceptible to attack by the solvent. Attempts are underway to prepare cation radical salts, and diazatetrathiafulvalenes bearing different substituents at C-3.

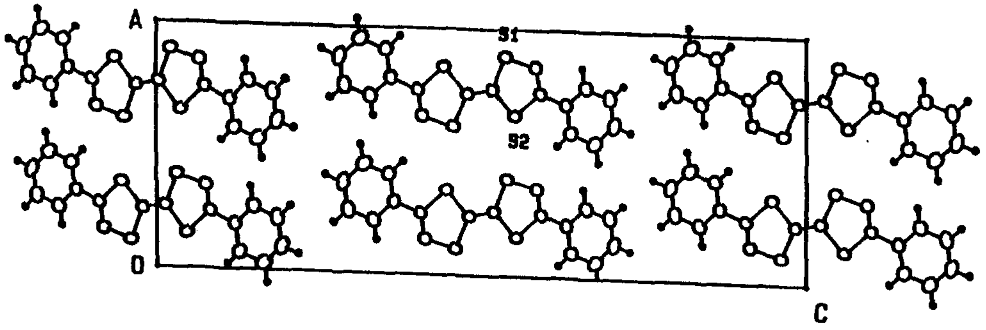


Fig. 2. The structure viewed along the *b* axis

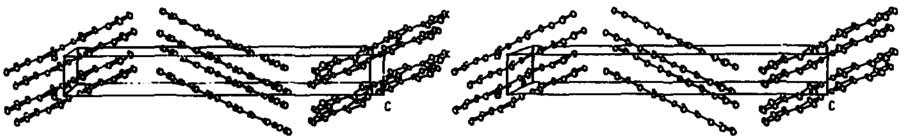


Fig.3. Stereoview showing the parallel stacking of the molecules as viewed along the *a* axis. Perpendicular spacing between molecules = 3.56 Å

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7. All new compounds gave satisfactory microanalyses. For the diphenyl derivative **5a**: δ_H ($CDCl_3$) 270 MHz 7.40-7.49(m) and 7.73-7.77(m) (ratio 3:2); δ_C($CDCl_3$) 67.93 MHz 128.03(d), 128.95(s,d), 131.39(d), 132.23(s) and 163.05(s) (ratio 2:3:1:1:1); *m/z* 358 (13%, M^+), 255 (20), 179 (2), 152 (10) and 103 (100); and ν_{max}(Nujol) 1519, 1240, 1075, 938, 797, 754 and 682 cm^{-1}.
8. Crystal data: $C_{16}H_{10}N_2S_4$, M_r 358.53, monoclinic, *C2/c*, a = 12.079 (4), b = 3.948 (1), c = 31.597 (10), β = 91.95 (3)°, V = 1506 (2), Z = 4, D_c = 1.581 g cm^{-3}, $\mu(MoK_\alpha)$ = 6.01 cm^{-1}, F (000) = 736, no. of parameters 100, no. of independent data 1872, 1355 with $|F_o| > 3\ \sigma\ |F_o|$, $R(R_w)$ = 0.032 (0.050). The maximum and minimum residues in the final ΔF synthesis were 0.288 and -0.251. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated MoK_α radiation at 297 K to $2\theta_{max}$ = 54°. Calculations were carried out using the Enraf-Nonius SDP package.[9] The structure was solved by direct methods and refined by full-matrix least-squares. All the non-hydrogen atoms were refined anisotropically, while the hydrogen atoms, generated geometrically, were not refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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12. Selected bond lengths (Å) and angles (°) in **5a**: S(1)-N 1.660(2), S(1)-C(1) 1.763(2), S(2)-C(1) 1.754(2), S(2)-C(2) 1.769, N-C(2) 1.283(2), C(2)-C(3) 1.467(3); N-S(1)-C(1) 98.59(9), C(1)-S(2)-C(2) 93.99(9), S(1)-N-C(2) 117.0(1), S(1)-C(1)-S(2) 111.2(2), and S(2)-C(2)-N 119.3(2).
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14. Thanks are due to the Croucher Foundation for financial support (for S.L.C.), and to the University of Hong Kong for a research grant.

(Received in Japan 21 September 1992)