The Stability of the Carbenes from 1,2-Dithiole and 1,3-Dithiole in Relation to the Synthesis of 1,1′,3,3′- and 1,1′,2,2′-Tetrathiafulvalenes

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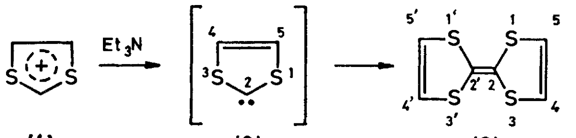
Calculations show that the carbene from 1,3-dithiole is a stable species, whereas that from 1,2-dithiole is thermodynamically unstable. From the results obtained, it is concluded that synthesis of 1,1′,2,2′-tetrathiafulvalene *via* carbenoid species is probably impossible.

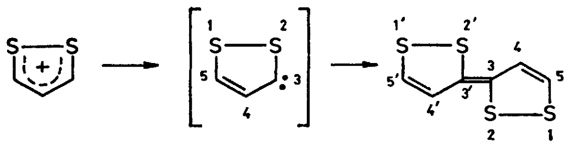
THE synthesis of 1,1′,3,3′-tetrathiafulvalene (3) (1,3-TTF) from the 1,3-dithiolylium salt (1) by deprotonation, probably *via* the carbene (2), was originally described by Prinzbach [1] and has since been used as a versatile synthesis for preparation of 1,3-TTFs,[2] a class of compounds which has recently attracted considerable interest as the donor in high conductivity organic donor–acceptor complexes.



(1) (2) (3)

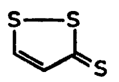
(1)

However, attempts to deprotonate the corresponding 1,2-dithiolylium salt (4) followed by dimerization of the carbene (5) to give 1,1′,2,2′-tetrathiafulvalene (6) (1,2-TTF) have been unsuccessful. The reaction results rather in formation of 1,2-dithiole-3-thiones [3] (7) or 1,6,6aλ^4-trithiapentalenes [4] (8). Neither was it possible to isolate 1,2-TTF from the Stevens–Bamford reaction of the tosylhydrazone (9) of 1,2-dithiol-3-one.[5] Rather, the various products formed by the thermolysis of (9) could be explained by assuming the transient existence of a short lived carbene from 1,2-dithiole.



(4) (5) (6)

(2)



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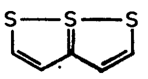

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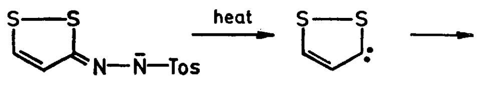
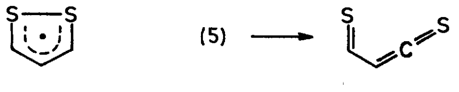


(9)

(6)

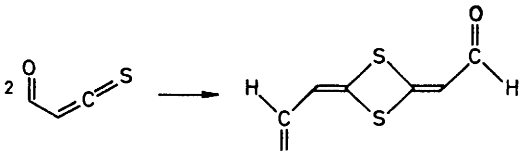
Since 1,2-TTFs recently have been prepared by methods, which probably involve 1,2-dithiolyl radicals (10),[6-8] the unsuccessful attempts to prepare (6) *via* carbenoid intermediates are most likely not due to the thermodynamic instability of (6), but rather either to the thermodynamic instability of (5), or perhaps a kinetically slow step leading to (6).

A thermodynamic explanation for the lack of success of the synthesis of 1,2-TTF by methods which give good results in the 1,3-dithiole series may be that the 1,2-dithiole carbene is less stable than the 1,3-dithiole carbene and reacts or decomposes before forming 1,2-TTF. One possibility is that the cyclic carbene (5) opens to give the thioacyl thioketen (11).



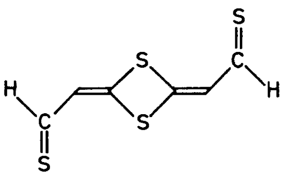
(10) (11)

In the 1,3-dithiole series this would not be expected, since the analogous reaction should involve the much more energetically costly breaking of a carbon–carbon bond. If such a thioacyl thioketen was to be formed there are several reasonable fates for which it might be destined. For instance, it is known that acyl thioketen (12) exists in the form of the dimeric derivative (desaurines) [9] (13).



(12) (13)

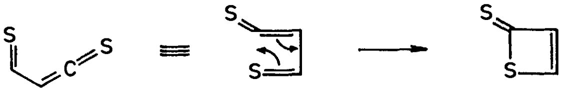
(3)



(14)

Although the corresponding thioxo-derivative (14) has never been isolated in reactions involving hypothetical 1,2-dithiole carbenes,[10] some of the products formed in the Stevens–Bamford reaction may be explained by reactions involving these thioxo-compounds,[5] leaving open the suggestion of the formation of (14) as an intermediate step in the decomposition of (11).

Alternatively, the thioacyl thioketen (11) could further decay by intramolecular cyclisation with formation of thiet-thione (15). It is thus of interest to study the stability of 1,3-TTF *versus* 1,2-TTF and the stability of 1,2-dithiole carbene *versus* the open-chain compound (11) or the cyclisation products (15) derived from this.


(4)

(15)

Calculations.—All calculations were performed with the semi-empirical CNDO/2 method using a standard program [11] as modified by Sabin *et al.*[12] The CNDO scheme is a semi-empirical method at the SCF level of approximation [13] in which certain coulomb and exchange integrals are semi-empirically parametrized and others are neglected. This method is known to produce reasonable reliable molecular geometries and should thus be applicable to the determination of the relative stabilities of the possible intermediates in the reactions leading to 1,2-TTF and 1,3-TTF. It should be remembered, however, that although the CNDO/2 method gives reliable geometries, heats of formation and bond energies tend to be greatly overestimated, and thus the energetics reported here should be taken as qualitatively rather than quantitatively meaningful.

A. *The* 1,1′,3,3′-*tetrathiafulvalene system.* Calculations were first carried out on 1,3-TTF. At the experimental equilibrium geometry [14] the CNDO/2 total energy is −87.252 209 a.u. The Mulliken gross atomic populations indicate that all atoms are nearly neutral, but indicate a slight shift of π-charge from the carbon to the sulphur atoms. There is some conjugation through the S(1)C(5)C(4)S(3) and S(1′)C(5′)C(4′)S(3′) systems, even though it seems to be smaller than conjugation through the carbon skeleton of 1,2-TTF (see Table 1). An increase in the C(2)C(2′) bond length gave a regularly increasing energy; this is expected as the molecule is stable with respect to cleavage of this bond.

TABLE 1

π-Bond orders of 1,2-TTF and 1,3-TTF with the numbering of the atoms indicated in equations (1) and (2)

	p_{12}	p_{23}	p_{34}	p_{45}	p_{15}	
cis-1,2-TTF (6)	0.05	−0.02	0.36	0.90	0.09	$p_{33'}$ 0.82
1,3-TTF (3)	0.03	0.03	0.25	0.95	0.25	$p_{22'}$ 0.88

Attention was then focused on the 1,3-TTF precursor, the carbene of 1,3-dithiole. The geometry of (2) was varied subject to the C_{2v} symmetry constraint. The minimum energy, −43.335 137 a.u., was obtained at the bond lengths *r*[C(4)C(5)] 1.364, *r*[C(2)S(1)] 1.744, and *r*[C(5)S(1)] 1.796 Å, which, relative to the geometry [14] of the same fragment of 1,3-TTF, indicates a slightly expanded ring. Calculations show that the 1,3-carbene is more stable in the singlet than in the triplet state which is as expected by analogy with calculations on other similar carbenes.[15]

The population analysis shows a shift in charge towards the carbene carbon atom, C(2), which is negative by 0.14e while C(5) and C(4) are positive by 0.08e. This charge shift is so small that it will not affect the ability of the 1,3-carbene to act as an electrophilic reactant.

Extensive geometry variations did not indicate the existence of other stable open or ring structures of (2) with lower energy than that reported above. It is thus likely that reaction (1) in fact does proceed *via* the 1,3-dithiole carbene. A comparison of total electronic energies, *i.e.* disregarding all kinetic effects, indicates that the last step in reaction (1) is highly exothermic (365 kcal mol^{-1}) as expected.

The actual mechanism for the formation of 1,3-TTF is probably a nucleophilic attack of one carbene on one dithiolylium ion with subsequent loss of a proton, and thus reaction (1) should not be construed as a mechanism.

Thus, the calculations give results entirely in agreement with the expected and observed behaviour of 1,3-TTF: it is stable with respect to C(2)C(2′) bond cleavage and is probably formed *via* the relatively stable cyclic 1,3-dithiole carbene.

B. *The* 1,1′,2′,2′-*tetrathiafulvalene system.* Attention was then turned to the 1,2-TTF system, where calculations similar to those done on 1,3-TTF were carried out. The geometry of the ring system in 1,2-TTF (6) was taken from an equivalent ring system in 4-acyl-1,2-dithiole-3-thione,[16] and was not further optimized. The length of the C(3)C(3′) bond connecting the two rings was then varied. The minimum energy corresponds to a C=C bond length of 1.37 Å, which is the same inter-ring bond length as in 1,3-TTF (3). The calculated ground state total energy of *cis*-1,2-TTF was −87.337 101 a.u. which was 0.118 kcal mol^{-1} lower than that of the *trans*-structure (this difference is so small that no conclusion can be drawn as to the relative stability of the two isomers of 1,2-TTF). As in the case of 1,3-TTF, the energy increases as the C(3)C(3′) bond is distorted from its equilibrium value indicating that the synthesis of 1,2-TTF probably does not fail due to thermodynamic instability of the product.

Mulliken population analysis shows that all atoms are essentially neutral with almost no charge transfer among the atoms. The π-bond orders (Table 1) show that the canonical structure with alternate single–double bond structure is reasonable, but that there is some conjugation through the carbon skeleton.

Since the 1,2-TTF seems itself to be thermodynamically stable, the question arises as to whether the 1,2-dithiole carbene can react or decompose in preference to dimerizing. Calculations were first performed on the

1,2-dithiole carbene (5) using the bond lengths and angles for the analogous rings as found in the 4-phenyl-1,2-dithiolylium ion.[17] Except for a slight increase in the S–S bond length this structure corresponded to the minimum energy geometry (see Table 2). However, in contrast to the calculations on the 1,3-carbene, the 1,2-carbene (5) can possibly form other stable configurations. For instance, cleavage of the S–S bond of (5) [*i.e.* reaction (3)] might be possible, leading to formation of the thioacyl thioketen (11), even though it is necessary to overcome a small energy barrier (*ca.* 25 kcal mol^{-1}) when breaking the bond. The thioketen structure corresponds to a metastable structure with the minimum energy given in Table 2. The minimum energy geometry for (11) is given in Figure 1 and the total energy of the *trans*-form is only 0.9 kcal mol^{-1} higher. Even though (11) is locally stable it is not lower in energy than (5), so reaction (3) is unlikely to proceed exothermically. To assess the stability of (11) relative to its dimeric product we calculated the total energy of the hypothetical thioxo-derivative (14). We used the geometry of the oxo-analogue [18] except that the C=S bond length was chosen to be 1.611 Å. The magnitude of the ground state energy of −87.170 319 a.u. indicates that the thioketens dimerize quite easily since this energy is 231 kcal mol^{-1} lower than that of two thioketen molecules. This is consistent with observations on bis(formylmethylene)-dithietan.[10] The total energy of bis(thioformylmethylene)dithietan is, however, substantially higher than that of the isoelectronic molecules 1,2-TTF and 1,3-TTF.

TABLE 2

Total CNDO/2 ground-state electronic energies for possible intermediates in the synthesis of 1,2-TTF (6)

Intermediate	(5)	(11)	(15)
Absolute (a.u.)	−43.409 337	−43.400 796	−43.480 251
Relative (kcal mol^{-1})	0.0	5.4	−44.5

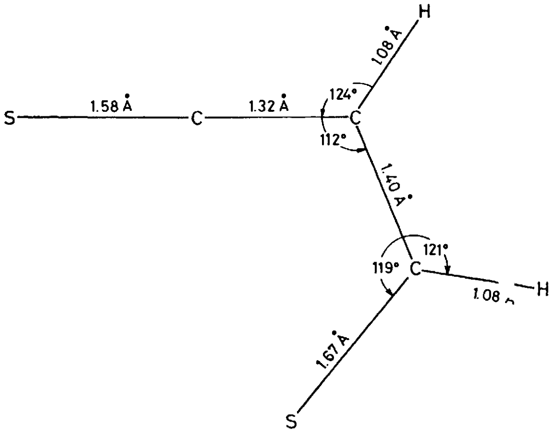


FIGURE 1 Calculated minimum energy geometry of the thioacyl thioketen (11)

In performing the calculations on the 1,2-carbene it was found that swinging the whole C=C=S fragment of the thioacyl thioketen inwards caused a reduction in energy (of *ca.* 25 kcal mol^{-1}). This led to an investigation of the stability of the hypothetical molecule thiet-2-thione (15) relative to the stability of (5). No structural data has been published for (15) or derivatives related to (15). The geometry used is shown in Figure 2, and has been constructed from structural data for compounds consisting of the same structural elements.[19-21] The energy of that molecule was substantially lower than that of the 1,2-carbene indicating that (15) is a more stable structure (see Table 2).

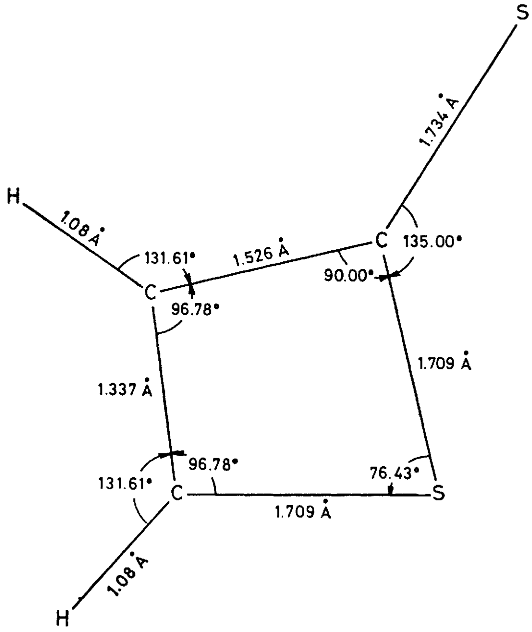


FIGURE 2 Geometry chosen for the calculation of the energy of thiet-2-thione (15)

The reason for the unsuccessful attempts to prepare 1,2-TTF by the carbene reaction (2) might thus be that the 1,2-carbene is unstable and rearranges into the more stable thiet-2-thione, a problem which is not present in the carbene reaction leading to 1,3-TTF. The total electronic energy of 1,2-TTF is substantially lower than that of two thiet-2-thione molecules so the calculation is not in contradiction with the fact that 1,2-TTF is a stable molecule, *i.e.*, the energetics do not favour the reaction (6) $\longrightarrow$ (5) $\longrightarrow$ (15). The structure of (15) as derived from the calculation is as expected. The gross atomic populations and the π-bond-order matrix for thiet-2-thione are given in Table 3. From these results we see that (15) shows conjugation through the S(1)C(2)S(2′)C(3) structure and that the C=S is polar, with S being the negative end.

Conclusions.—We have performed CNDO/2 calculations on possible intermediates in the reactions leading to 1,2-TTF (6) and 1,3-TTF (3) *via* carbenes. The calculations predict that the 1,3-dithiole carbene (2) is a relatively stable species whereas 1,2-dithiole carbene (5) can decay into the more stable thiet-2-thione (15) or perhaps the thioxo-derivative (14). It should thus be possible to prepare 1,3-TTF by a carbene-type reaction, but the same should not be possible for 1,2-TTF. Both these observations are in agreement with experimental observations.

It has been observed that 1,2-TTF is thermally less stable than 1,3-TTF. On heating, 1,2-TTF loses two sulphur atoms forming thieno[3,2-*b*]thiophen.[7] In the mass spectra of 1,2-TTF the most prominent peaks are due to the loss of one or two sulphur atoms from the molecular ion. Field-ionization mass spectra indicate that these peaks are formed by pyrolysis before ionization.[22] The same has never been observed for 1,3-TTF.[23]

TABLE 3

Mulliken gross atomic populations q relative to the neutral atoms (in units of electronic charge) and π-bond orders p for thiet-2-thione (15) with numbering given in equation (4)

q_1	q_2	$q_{2'}$	q_3	q_4
−0.11	−0.11	0.17	0.04	−0.05
p_{12}	$p_{22'}$	p_{23}	p_{34}	p_{41}
0.35	0.70	0.33	0.91	0.01

These observations are not contradictory to the calculation, which shows that 1,2-TTF is more stable than 1,3-TTF by some 50 kcal mol^{-1}.

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