Topochemical Double Photocyclodimerization of Bis(butoxycarbonyl)-Substituted Tetrathiafulvalene in the Crystalline State

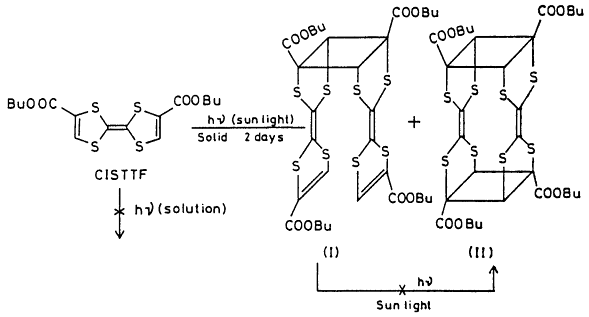
P. VENUGOPALAN and K. VENKATESAN*
Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India

(Received October 5, 1989)

Crystals of bis(butoxycarbonyl)-substituted tetrathiafulvalene having three reactive double bonds yield upon irradiation two products, a "cage product" (**II**) as well as another (**I**) by the participation of a pair of reactive double bonds. The formation of both the products is understood based on the molecular packing in the crystal lattice. The circumstances leading to the formation of more than one photoproduct in the crystalline state and the question regarding the sulfur atom as a steering group in the context of crystal engineering are discussed.

In the crystalline state photocyclodimerizations, the rate of the reaction as well as the nature of the products obtained are governed by the packing characteristics, local symmetry and the separation distance between the reactive double bonds.[1–3] The main problem in achieving photochemical reactions in crystalline state is to bring the reactive partners close enough (≈4 Å) in the crystal lattice. To achieve this goal attempts are made to discover suitable steering groups. For example, it has been observed that chlorine is, by and large, a good steering group leading to, more often than not, the β type packing.[4,5] The suggestion that sulfur could also be a good steering group emanates from the observation that molecules containing divalent sulfur atoms reveal intermolecular S...S contacts less than 3.7 Å in the crystal lattice.[6,7]

In this connection, it is interesting that bis(butoxycarbonyl)-substituted tetrathiafulvalene ((*Z*)-4,4′-bis(butoxycarbonyl)-$\Delta^{2,2'}$-bi-1,3-dithiole: CISTTF) undergoes a solid state photochemical [2+2] cycloaddition reaction.[8] It is noteworthy that two products have been obtained (Scheme 1). However, there is no reaction in the solution phase. It has also been observed that crystals of the trans isomer, namely (*E*)-4,4′-bis(butoxycarbonyl)-$\Delta^{2,2'}$-bi-1,3-dithiole (TRATTF) do not undergo dimerization. In order to understand the difference in the photochemical behavior of these two derivatives with three reactive double bonds as well as to assess the possible role of sulfur atoms in the reactive compound, three dimensional crystallographic investigation of these two compounds were carried out. We became aware recently that the structure determination of TRATTF has been reported.[9] So we confine ourselves to discuss the results pertaining to CISTTF only.



Scheme 1.

Experimental

Both the isomers of tetrathiafulvalenecarboxylic esters were synthesized as per the reported procedures.[10,11] Finely powdered CISTTF (80 mg; 20 mmol) was taken in a sealed glass tube and kept in sunlight for 2 days. The sample was shaken from time to time. During the irradiation, deep orange color of the compound changed to yellow. TLC analysis of the resulting yellow compound did not reveal the presence of any polymeric material. Chromatography on a column of silica gel (particle size 0.2—0.5 mm; length 20 cm; diameter 1 cm) packed with hexane and elution with chloroform-hexane (70 : 30) gave the first fraction as the 'cage product' (**II**) (52 mg; 65%) and second fraction as (**I**) (24 mg; 30%). They were characterized and the physical data were in good agreement with the earlier study.[8].

Structural Investigation. Good single crystals of CISTTF were obtained from ethanol-chloroform (70 : 30) by slow evaporation. Preliminary rotation and Weissenberg photographs indicated that the crystal system is monoclinic. Crystal data: $C_{16}S_4O_4H_{20}$, M=404.2, space group, $P2_1/a$, a=8.663(2), b=26.745(4), c=8.941(1) Å, β=108.24(2)°, V=1967.5 Å^3, Z=4, d_x=1.36 g cm^{-3}, d_m=1.35 g cm^{-3}. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using a crystal of 0.4×0.3×0.15 mm size in ω-2θ mode with a scan speed of 1° min^{-1} upto $\theta \leq 70°$ (λ=1.5418 Å). The cell parameters were determined accurately by least squares analyses of 25 standard reflections in the range $10° < \theta < 31°$. The stability and orientation of the crystal were monitored by using three standard reflections after every 1800 s of X-ray exposure, the orientation was checked once in 100 reflections. The three monitored reflections (161, $0\bar{3}\bar{1}$, 250) showed only statistical variations within 2%. 3822 reflections were collected, 3205 unique R_{int}=0.066, 2599 siginificant reflections with $[|F_o| > 3\sigma(|F_o|)]$. Corrections were applied for Lorentz and polarization factors and for absorptions (μ=43.3 cm^{-1}).[12]

The structure was solved using direct method program MULTAN-84.[13] At the isotropic convergence stage it was found that the three terminal atoms of one of the side chains namely (C(14),C(15),C(16)) and the methyl carbon of the other side chain (C(8)) were disordered. Full matrix least squares refinements[14] of scale factor, positional and anisotropic thermal parameters of non-hydrogen atoms without disorder as well as positional and isotropic thermal parameters of disordered atoms was performed. As for the hydrogen atoms, they were refined for their positional and isotropic thermal parameters. The final R=0.069 and R_w=0.077. The function minimized in the least squares refinement was $\Sigma(w|F_o|-|F_c|)^2$ where $w=k/(\sigma^2|F_o|)+g|F_o|^2)$ with k=1.9290 and g=0.002014. The final difference Fourier map was featureless. Residual electron density in the final ΔF was less than 0.4 eÅ^{-3}. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[15]

Results and Discussion

Positional coordinates of non-hydrogen atoms are listed in Table 1.[16] Selected bond lengths and angles are recorded in Table 2. A perspective view of the molecule drawn with ORTEP[17] along with numbering scheme is shown in Fig. 1. The tetrathiafulvalene (TTF) moiety is nearly planar in the title compound (CISTTF) with a small twist about C(1)-C(9), the angle between the least squares planes passing through both the five membered rings being 2.3(2)°. Atoms C(2) and C(3) deviate significantly from the least squares plane defined by S(1), S(2), C(1), C(9), S(3), and S(4): (C(2)=0.071(5); C(3)=0.072(5) Å) whereas C(10) and C(11) lie in the plane. Thus TTF moiety in CISTTF has a sofa conformation as against the chair conformation observed in TRATTF[9] or

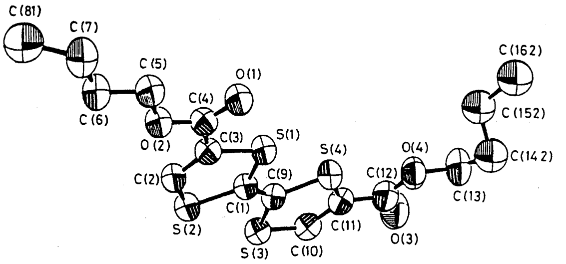


Fig. 1. A perspective view of the molecule with atomic numbering scheme and the thermal ellipsoids at 50% probability level. Disordered atoms with less occupancy are not shown.

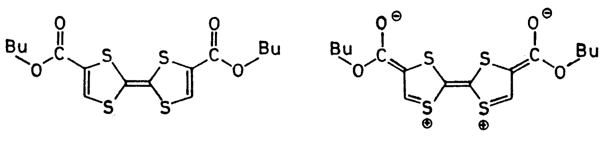
Table 1. Fractional Atomic Coordinates (×10^4) and Equivalent Temparature Factors (×10^4) for Non-Hydrogen Atoms with e.s.d.'s in Parentheses

$$U_{eq}=(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$$

	x	y	z	U_{eq}
S(1)	2245(1)	517(0)	9160(1)	745(4)
S(2)	3518(2)	−282(0)	11516(1)	765(6)
S(3)	6355(2)	486(0)	13532(1)	766(4)
S(4)	5040(2)	1260(0)	11101(1)	789(4)
O(1)	−562(4)	244(1)	6484(4)	799(12)
O(2)	−669(4)	−565(1)	7136(4)	776(12)
O(3)	8627(6)	2048(2)	13816(5)	1278(19)
O(4)	6529(4)	2205(1)	11665(4)	904(14)
C(1)	3710(5)	338(2)	10934(5)	653(15)
C(2)	1897(6)	−421(1)	9904(5)	719(17)
C(3)	1309(6)	−66(2)	8821(5)	660(15)
C(4)	−58(5)	−109(2)	7355(5)	680(16)
C(5)	−2011(6)	−647(2)	5677(6)	825(19)
C(6)	−2390(7)	−1188(2)	5573(6)	949(23)
C(7)	−3691(10)	−1316(2)	4053(7)	1226(30)
C(81)	−3665(22)	−1894(6)	3642(17)	1291(48)
C(82)	−4447(19)	−1846(6)	4009(18)	1219(45)
C(9)	4870(6)	648(2)	11755(5)	676(13)
C(10)	7320(6)	1052(2)	13798(5)	784(18)
C(11)	6731(6)	1411(2)	12699(5)	734(17)
C(12)	7417(7)	1914(2)	12813(6)	891(21)
C(13)	7050(9)	2723(2)	11680(8)	1189(28)
C(141)	6310(20)	2925(6)	9971(14)	1035(46)
C(142)	5779(13)	3042(4)	10757(12)	1035(28)
C(151)	4616(24)	2997(7)	9490(21)	1243(51)
C(152)	5665(19)	2898(6)	9110(17)	1346(44)
C(161)	3720(18)	3306(6)	8081(17)	1265(41)
C(162)	4485(26)	3251(8)	7699(23)	1394(64)

Table 2. Selected Bond Lengths (l) and Angles (ϕ) Involving Non-Hydrogen Atoms with Their e.s.d.'s in Parentheses

Distance	l/Å	Distance	l/Å	Angle	ϕ/°	Angle	ϕ/°
S(1)-C(1)	1.759(4)	O(4)-C(13)	1.453(6)	C(1)-S(1)-C(3)	94.6(2)	O(2)-C(5)-C(6)	107.4(4)
S(1)-C(3)	1.739(5)	C(1)-C(9)	1.331(7)	C(1)-S(2)-C(2)	94.8(2)	C(5)-C(6)-C(7)	111.6(5)
S(2)-C(1)	1.763(5)	C(2)-C(3)	1.337(6)	C(9)-S(3)-C(10)	95.5(2)	C(6)-C(7)-C(81)	111.7(8)
S(2)-C(2)	1.709(5)	C(3)-C(4)	1.471(6)	C(9)-S(4)-C(11)	94.6(2)	S(3)-C(9)-S(4)	114.6(3)
S(3)-C(9)	1.757(5)	C(5)-C(6)	1.480(8)	C(4)-O(2)-C(5)	116.0(4)	S(3)-C(9)-C(1)	124.0(4)
S(3)-C(10)	1.710(5)	C(6)-C(7)	1.509(9)	C(12)-O(4)-C(13)	116.7(4)	S(4)-C(9)-C(1)	121.4(4)
S(4)-C(9)	1.760(5)	C(7)-C(81)	1.591(17)	S(1)-C(1)-S(2)	114.4(3)	S(3)-C(10)-C(11)	118.1(4)
S(4)-C(11)	1.744(5)	C(7)-C(82)	1.555(19)	S(1)-C(1)-C(9)	122.5(4)	S(4)-C(11)-C(10)	117.3(4)
O(1)-C(4)	1.213(6)	C(10)-C(11)	1.355(7)	S(2)-C(1)-C(9)	123.1(4)	S(4)-C(11)-C(12)	119.3(4)
O(2)-C(4)	1.320(6)	C(11)-C(12)	1.461(8)	S(2)-C(2)-C(3)	118.9(4)	C(10)-C(11)-C(12)	123.3(5)
O(2)-C(5)	1.467(6)	C(13)-C(141)	1.558(14)	S(1)-C(3)-C(2)	117.3(4)	O(3)-C(12)-O(4)	124.1(5)
O(3)-C(12)	1.201(7)	C(13)-C(142)	1.433(14)	S(1)-C(3)-C(4)	115.2(4)	O(3)-C(12)-C(11)	124.6(5)
O(4)-C(12)	1.326(6)	C(141)-C(151)	1.407(27)	C(2)-C(3)-C(4)	127.5(5)	O(4)-C(12)-C(11)	111.3(5)
C(142)-(152)	1.495(20)	C(151)-C(161)	1.504(24)	O(1)-C(4)-O(2)	125.2(4)	O(4)-C(13)-C(141)	106.9(7)
C(152)-C(162)	1.649(24)			O(1)-C(4)-C(3)	122.7(4)	C(13)-C(141)-C(151)	114.6(13)
				O(2)-C(4)-C(3)	112.1(4)	C(141)-C(151)-C(161)	123.1(16)



Scheme 2.

in other TTF derivatives such as $\Delta^{2,2'}$-bis-1,3-benzodithiole[18] and diphenyltetrathiafulvalene.[19] In the case of bis(ethylenedithio)tetrathiafulvalene the molecule occupies a nonplanar conformation in the crystal lattice.[20] Another striking feature is that the C-S bond lengths S(3)-C(10) (1.710(5)) and S(2)-C(2) (1.709(5) Å) are significantly shorter than S(4)-C(11) (1.744(5) Å) and S(1)-C(3) (1.739(5) Å). The observed bond length variation indicates that the following valence bond structures are important (Scheme 2).

This trend in the C-S bond lengths is observed in substituted TTFs with electron-withdrawing groups attached to it. For example, the C-S bond lengths in TRATTF are 1.749(2) and 1.725(2) Å.[9] In diphenyltetrathiafulvalene[19] the C-S bond length in the phenyl-substituted side is longer (1.777(7) Å) than the unsubstituted side (1.739(7) Å). This trend is not observed in TTF derivatives which are symmetrically substituted.[20]

Structure Reactivity Correlation. From the packing diagram (Fig. 2), it is observed that the nearest neighbouring molecules are related by an inversion center. The two potentially reactive pairs of double bonds (C(2)=C(3) and C(10)=C(11)) with nearest neighbours are placed at a distance of 3.944 Å (C(2)...C(11)) and 3.947 Å ((C(3)...C(10)) in the crystal lattice. For the [2+2] photodimerization to occur, the π orbitals of the reactive double bonds would, in the ideal situation, be expected to overlap. The geometrical parameters of relevance are center-to-center distance between the reactive double bonds, angles $\theta_1,\theta_2,\theta_3$, and the displacement of the double bonds, d, with respect to one another (Fig. 3).

For the best overlap of the π orbitals for the cyclodimerization $\theta_1=0°$, $\theta_2=\theta_3=90°$, and $d=0$ Å. The calculated values are $\theta_1=0°$, $\theta_2=80.6°$, $\theta_3=62.2°$, and $d=1.81$ Å. Thus considerable motion of the reactive partners are required before the reaction ensues.

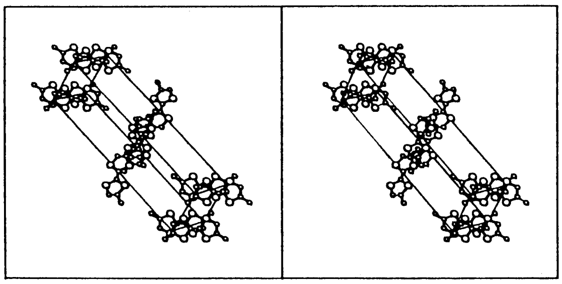


Fig. 2. Stereo packing of the molecules in the unit cell. The side chains are not shown for clarity.

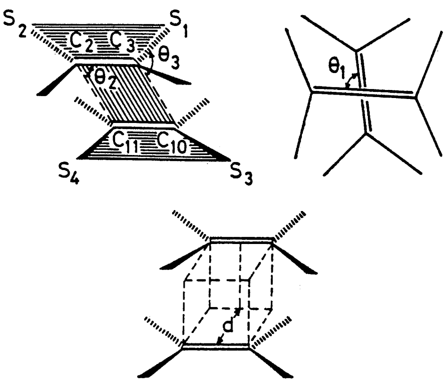


Fig. 3. Geometrical parameters used in the relative representation of the reactive double bonds.

Indeed, it has been noted that in most of the photoreactive compounds, the ideal geometrical conditions are not achieved.[5] These observations emphasize that there must be sufficient cavity volume available in the crystal lattice which could permit the necessary motions of the reactive partners so as to achieve the overlap of the orbitals upon excitation.

From the packing of the molecules (Fig. 2) it is clear that the bonds C(10)=C(11) and its centrosymmetrically related partner C(2)=C(3) would interact to produce the experimentally observed double [2+2] photocyclodimerization product. It has been reported that in addition to the 'cage product' (**II**), another dimer (**I**) also was obtained.[8] It may be mentioned that according to Kreitsberga et al.[8] the yield of **II** is only 12% whereas the yield of **I** is as high as 70%. However according to our experiment the major product corresponds to **II**, 65% yield, and **I** is 30%. A stepwise mechanism in which the cage product could result from **I** is ruled out as the irradiation of **I** does not yield **II**. It is possible that in some reaction sites, as one pair of double bonds interact, the other pair would be expected to move too far apart resulting in unfavourable orientation of the other partner. The occurrence of more than one product with significant yields in a topochemically controlled solid state reaction is exceptional. In this connection two observations reported in literature are noteworthy. In the photoreaction of dimethyl (2*E*,5*E*)-4-oxo-2,5-heptadienoate in the solid state, it has been observed that a single product with two cyclobutane rings was obtained.[21] On the other hand, photoirradiation of 1,4-dicinnamoylbenzene produces, in high yield, a double [2+2] cycloaddition product and a small amount of oligomers.[22] Another important observation is that the photoirradiation of unsymmetrically substituted diolefin compounds such as α-cyano-4-[2-(4-pyridyl)-ethenyl]cinnamates resulted in dimers and oligomers in the solid state which could be rationalized in terms of their molecular packing.[23] The molecular packing in the title compound permits neither the formation of oligomers nor the photodimerization between

C(1)=C(9) and its centrosymmetrical partner.

In many of the crystal structures containing divalent sulfur, the sulfur atoms act as electrophile-nucleophile couple having short intermolecular contacts less than 3.70 Å.[6,7] In the title compound, however, the shortest S...S distance between the reacting molecules is 3.95 Å, significantly longer than the sum of van der Waals radii (3.70 Å). This observation is in agreement with other neutral tetrathiafulvalene derivatives.[18,19,24–26] Thus the role of S atoms in steering the molecules is not clearcut and not, at any rate, the only controlling factor. In this connection it is noteworthy that the crystals of the trans isomer are not photoreactive at all. It may be mentioned that the role of chlorine as a steering group is beyond question[27–31] although it appears that it is not effective for all kinds of molecular framework.[32]

To conclude, while the present study allows us to rationalize the photochemical behavior of CISTTF, the role of sulfur atoms for crystal engineering could not be substantiated in the present case as well as in the case of the photostable TRATTF. The results of the present study as well as a few other reports in the literature[21–23] reveal that in molecules containing more than one reactive double bond, the solid state photoreaction yields more than one product, the singular exception being dimethyl (2*E*,5*E*)-4-oxo-2,5-heptadienoate in which one product is obtained.[21] The factors controlling this observation appear to be the subtle features of the molecular packing within the broad classification of the α and β type packing modes as well as the degree of molecular motions that the particular crystal would permit.

The authors thank the Council of Scientific and Industrial Research and the University Grants Commission, Government of India, for financial support.

References

1) M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, **1964**, 1996.

2) M. D. Cohen, G. M. J. Schmidt, and F. J. Sonntag, *J. Chem, Soc.*, **1964**, 2000.

3) G. M. J. Schmidt, *J. Chem. Soc.*, **1964**, 2014.

4) M. D. Cohen, B. S. Green, Z. Ludmer, and G. M. J. Schmidt, *Chem. Phys. Lett.*, **7**, 486 (1970).

5) V. Ramamurthy and K.Venkatesan, *Chem. Rev.*, **87**, 433 (1987).

6) R. E. Rosenfield, R. Parthasarathy, and J. D. Dunitz, *J. Am. Chem. Soc.*, **99**, 4860 (1977).

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

8) Ya. N. Kreitsberga, E. E. Liepinsh, I. B. Mazheika, and O. Ya. Neiland, *J. Org. Chem. USSR., Eng. Transl.*, **22**, 367 (1986).

9) R. M. Lobkovskaya, R. P. Shibaeva, Ya. N. Kreitsberga, and O. Ya. Neiland, *Sov. Phys. Crystallogr., Eng. Transl.*, **30**, 469 (1985).

10) Cu. Pittman Jr, M. Narita, and Y. F. Liang, *J. Org. Chem.*, **41**, 2855 (1976).

11) S. Yoneda, T. Kawase, M. Inaba, and Z. Yoshida, *J. Org. Chem.*, **43**, 595 (1978).

12) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **24**, 351 (1968).

13) P. Main, G. Germain, and M. M. Woolfson, MULTAN-84: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction data, University of York, England (1984).

14) G. M. Sheldrick, SHELX-76: A Program for Crystal Structure Determination, University of Cambridge (1976).

15) "International Tables for X-ray Crystallography," Vol IV, Kynoch Press, Birmingham (1974).

16) The tables of anisotropic temperature factors for non-hydrogen atoms, the atomic and thermal parameters of hydrogen atoms and the F_o-F_c are deposited as Document No. 8922 at the Office of the Editor of Bull. Chem. Soc. Jpn.

17) C. K. Johnson, ORTEP-II Report ORNL-5138, Oak-Ridge National Laboratory, Tennessee, 1976.

18) R. P. Shibaeva, R. M. Lobkovaskaya, and V. N. Klyuev, *Cryst. Struct. Commun.*, **11**, 835 (1982).

19) A. Escande and J. Lapasset, *Cryst. Struct. Commun.*, **8**, 1009 (1979).

20) H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **59**, 301 (1986).

21) B. S. Green and G. M. J. Schmidt, *Tetrahedron Lett.*, **49**, 4249 (1970).

22) M. Hasegawa, K. Saigo, T. Mori, H. Uno, M. Nohara, and H. Nakanishi, *J. Am. Chem. Soc.*, **107**, 2788 (1985).

23) M. Hasegawa, Y. Endo, M. Aoyama, and K. Saigo, *Bull. Chem. Soc. Jpn.*, **62**, 1556 (1989).

24) W. F. Cooper, N. C. Kenny, J. W.Edmonds, A. Nagel, F. Wudl, and P. Coppens, *J. Chem. Soc., Chem. Commun.*, **1971**, 889.

25) V. K. Belsky and D. Voet, *Acta Crystallogr., Sect. B*, **32**, 272 (1976).

26) L. Ouahab and P. Batail, *Acta Crystallogr., Sect. C*, **41**, 928 (1985).

27) G. M. J. Schmidt, *J. Pure Appl. Chem.*, **27**, 647 (1971).

28) K. Gnanaguru, G. S. Murthy, K. Venkatesan, and V. Ramamurthy, *Chem. Phy. Lett.*, **109**, 255 (1984).

29) W. Jones, S. Ramdas, C. R. Theocharis, J. M. Thomas, and N. W. Thomas, *J. Phys. Chem.*, **85**, 2594 (1981).

30) G. R. Desiraju, and J. A. R. P. Sharma, *Acc. Chem. Res.*, **19**, 222 (1986).

31) N. Ramasubbu, R. Parthasarathy, and P. M. Rust, *J. Am. Chem. Soc.*, **108**, 4308 (1986).

32) K. Venkatesan and P. Venugopalan, **1989**, Unpublished results.