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CYCLOADDITION TO 3H-1,2-DITHIOLE-3-THIONES. X-RAY STRUCTURAL INVESTIGATION OF 2,3,4′,5′-TETRACARBOMETHOXY-5-METHYL-6-PHENYLTHIOPYRAN-4-SPIRO-2′-(1,3-DITHIOLE)

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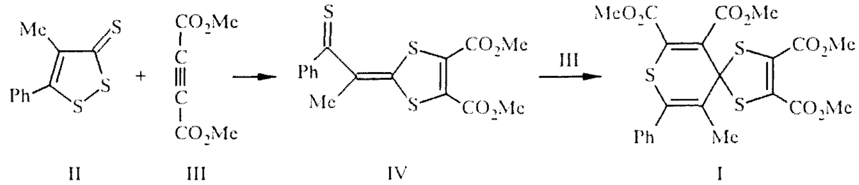
Treatment of 4-methyl-5-phenyl-3H-1,2-dithiole-3-thione with dicarbomethoxyacetylene gave 2,3,4′,5′-tetracarbomethoxy-5-methyl-6-phenylthiopyran-4-spiro-2′-(1,3-dithiole) whose structure was proved by x-ray investigation.

Continuing studies of spirocyclic structures containing the spiro atom bound to several sulfur atoms [1], we have synthesized 2,3,4′,5′-tetracarbomethoxy-5-methyl-6-phenylthiopyran-4-spiro-2′-(1,3-dithiole)(I) via a two stage reaction of 4-methyl-5-phenyl-3H-1,2-dithiole-3-thione (II) with dicarbomethoxyacetylene (III).



In the classification of Zefirov and Trach [2], the first stage is a [2′+(1,5)] sigmatropic addition. The dark green adduct of 4,5-dicarbomethoxy-2-(α-thiobenzylethylidene)-1,3-dithiole (IV) formed in this stage has previously been described by us [3] and it reacts readily with a second molecule of ester III by a hetero-[4+2]-cycloaddition [4-6] to give the light yellow spyran I.

The structure of I was proved by x-ray crystallographic analysis.*

Compound I has two crystallographically independent forms, differing in their orientation of the substituents on the six membered ring. Figure 1 shows a general view and numbering for one of these forms and Figure 2, a superposition of both molecules about the $C_4C_5S_3C_6C_7$ fragment. Figure 2 clearly shows that the two forms differ in the orientation of the phenyl rings (torsional angles for $S_3C_5C_{13}C_{14}$ of 99.5 and 87.5°) and the carbomethoxy groups (torsional angles 74.4 and −99.7°). There is also a slight difference in the spiro angle orientation of the five membered heterocycles (torsional angles $C_6C_7C_1S_1$ and $C_7C_1S_1C_2$ being 118.1 and 106.5 and 109.2 and 125.3° in the two forms). Because the two molecules differ little in the remaining geometry, average values for the bond lengths and valence angles are given in subsequent discussion.

The conformation of the six membered heterocycle in both molecules can be described as a strongly flattened boat with a twist angle about the S_3-C_1 axis of 4.0 and 6.9°. One of the carbomethoxy groups (at C_7) is virtually perpendicular to the heterocycle plain whereas the one at C_6 is collinear with this plane and is conjugated with the $C_6=C_7$ double bond. This is reflected in the shortening of the $C_6=C_{19}$ bond length to 1.500 Å when compared with the $C_7=C_{21}$ length of 1.523 Å.

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*Numbering for I differs from standard nomenclature.

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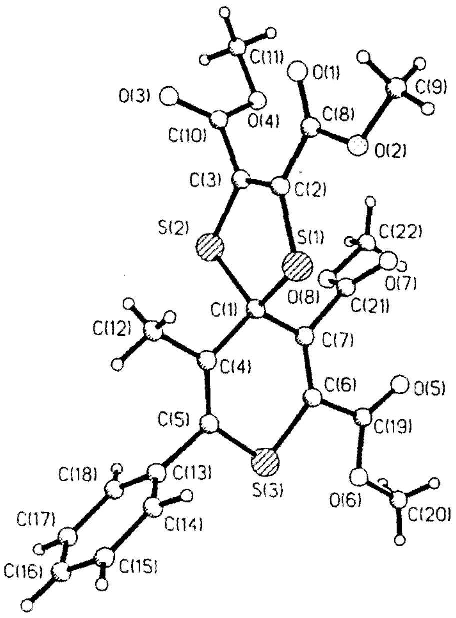

Fig. 1. Overall view and numbering of the atoms in one of the independent molecules of compound I.

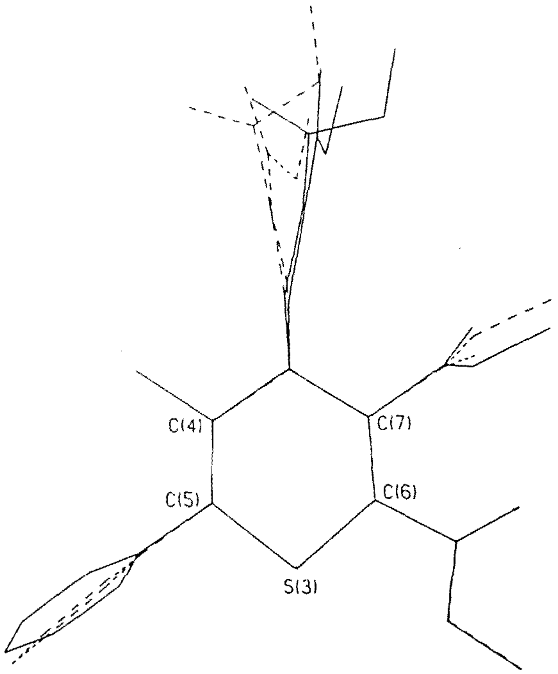

Fig. 2. Two independent molecules of I with the $S_3C_4C_5C_6C_7$ fragments superposed.

The five-membered 1,3-dithiole ring has the conformation of a C_1-envelope with a twist angle about the S_1-S_2 axis of 12.0 and 10.6°. It should be noted that structural studies of compounds containing a 1,3-dithiole ring with an sp^3 hybridized carbon at position 2 are very few. The Cambridge Crystallographic Database [7] contains data for only two such structures [8, 9]. In both cases, the displacement of the five membered ring (23-29°) is significantly greater that in molecule I. Evidently, the flattening of the dithiole rings in I is due to packing effects since the geometry of all three structures is virtually identical

TABLE 1. Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors U (Å $\times$ 10^3) for the Nonhydrogen Atoms in I

Atom	x	y	z	U
1	2	3	4	5
$S_{(1)}$	1101(1)	7226(1)	1417(1)	25(1)
$S_{(2)}$	1240(1)	5709(1)	2169(1)	30(1)
$S_{(3)}$	4529(1)	6649(1)	2224(1)	26(1)
$O_{(1)}$	-1833(3)	6641(2)	882(2)	46(1)
$O_{(2)}$	-875(2)	7590(2)	578(1)	33(1)
$O_{(3)}$	-1247(3)	5441(2)	2171(2)	71(2)
$O_{(4)}$	-986(2)	4922(2)	1229(1)	35(1)
$O_{(5)}$	3825(3)	5586(2)	520(2)	58(2)
$O_{(6)}$	5248(3)	5961(2)	1251(1)	38(1)
$O_{(7)}$	1520(3)	5982(2)	369(1)	46(1)
$O_{(8)}$	2179(3)	4932(2)	967(1)	45(1)
$C_{(1)}$	2035(3)	6505(2)	1907(2)	20(1)
$C_{(2)}$	-21(3)	6658(2)	1340(2)	22(1)
$C_{(3)}$	49(3)	5982(2)	1676(2)	25(2)
$C_{(4)}$	2659(4)	6897(2)	2549(2)	24(2)
$C_{(5)}$	3683(3)	6940(2)	2709(2)	21(2)
$C_{(6)}$	3691(4)	6206(2)	1544(2)	22(2)
$C_{(7)}$	2671(4)	6152(2)	1457(2)	24(2)
$C_{(8)}$	-1013(4)	6948(2)	922(2)	26(2)
$C_{(9)}$	-1799(4)	7887(3)	121(2)	42(2)
$C_{(10)}$	-821(4)	5436(2)	1719(2)	32(2)
$C_{(11)}$	-1776(4)	4343(3)	1255(3)	43(2)
$C_{(12)}$	2010(4)	7214(3)	3004(2)	35(2)
$C_{(13)}$	4303(3)	7257(2)	3364(2)	20(1)
$C_{(14)}$	4439(4)	8052(2)	3480(2)	35(2)
$C_{(15)}$	5064(4)	8311(3)	4079(2)	43(2)
$C_{(16)}$	5546(4)	7792(3)	4562(2)	38(2)
$C_{(17)}$	5409(4)	7004(2)	4454(2)	36(2)
$C_{(18)}$	4796(4)	6739(2)	3854(2)	28(2)
$C_{(19)}$	4238(4)	5873(2)	1048(2)	26(2)
$C_{(20)}$	5890(5)	5615(3)	852(3)	44(2)
$C_{(21)}$	2050(4)	5694(2)	859(2)	28(2)
$C_{(22)}$	1725(6)	4450(3)	386(3)	62(3)
$S_{(1')}$	-6087(1)	-8282(1)	-1388(1)	24(1)
$S_{(2')}$	-6244(1)	-9737(1)	-2225(1)	29(1)
$S_{(3')}$	-9466(1)	-8552(1)	-2206(1)	27(1)
$O_{(1')}$	-3135(3)	-8515(2)	-1318(2)	42(1)
$O_{(2')}$	-4054(2)	-7891(2)	-679(1)	31(1)
$O_{(3')}$	-3975(3)	-9676(2)	-2669(2)	53(1)
$O_{(4')}$	-3712(2)	-10260(1)	-1665(1)	29(1)
$O_{(5')}$	-8885(3)	-9780(2)	-585(1)	41(1)
$O_{(6')}$	-10279(2)	-9305(2)	-1299(1)	30(1)
$O_{(7')}$	-7320(3)	-10609(2)	-1129(1)	43(1)
$O_{(8')}$	-6654(2)	-9613(2)	-461(1)	33(1)
$C_{(1')}$	-7031(3)	-8950(2)	-1954(2)	21(2)
$C_{(2')}$	-4951(3)	-8688(2)	-1533(2)	23(2)
$C_{(3')}$	-5029(3)	-9328(2)	-1919(2)	24(2)
$C_{(4')}$	-7591(3)	-8475(2)	-2564(2)	24(2)
$C_{(5')}$	-8582(3)	-8292(2)	-2682(2)	22(2)

and shortening of intramolecular contacts involving peripheral atoms of the five membered rings in I is absent. In structure I there are a series of short intermolecular contacts: $O_1 \ldots C_{22'}$ (−x, 1 − y, −z) 3.225; $O_3 \ldots C_{14'}$ (−x − 1, −y, −z) 3.230; $O_3 \ldots C_{14'}$ (−x, −y − 1, −z) 3.233 Å. These possibly lead to both flattening of the dithiole ring and to differing orientation in the two isomers of I.

An interesting feature of the structure of the dithiole ring in I is the non-equivalence in S−C (sp^2) bond lengths (1.754(5) and 1.736(4) Å). The cause is the asymmetric orientation of the CO_2Me groups with respect to the heterocycle. One of these (at C_2) lies in the plane of the endocyclic C=C double bond and is conjugated with its π-system. The second is displaced from conjugation (torsional angles for $C_2C_3C_{10}O_3$ are −96.1 and −100.0°). A contribution to the observed geometry

TABLE 1 (continued)

1	2	3	4	5
$C_{(6')}$	-8699(3)	-9146(2)	-1594(2)	20(2)
$C_{(7')}$	-7707(4)	-9311(2)	-1539(2)	22(2)
$C_{(8')}$	-3938(4)	-8355(2)	-1182(2)	27(2)
$C_{(9')}$	-3114(4)	-7630(3)	-215(2)	40(2)
$C_{(10')}$	-4171(4)	-9751(2)	-2129(2)	27(2)
$C_{(11')}$	-2921(4)	-10737(3)	-1847(3)	44(2)
$C_{(12')}$	-6924(4)	-8206(3)	-3018(2)	35(2)
$C_{(13')}$	-9145(3)	-7770(2)	-3232(2)	22(1)
$C_{(14')}$	-9174(4)	-6975(2)	-3115(2)	28(2)
$C_{(15')}$	-9770(4)	-6489(3)	-3587(2)	38(2)
$C_{(16')}$	-10336(4)	-6789(3)	-4180(2)	42(2)
$C_{(17')}$	-10304(4)	-7580(3)	-4308(2)	42(2)
$C_{(18')}$	-9721(4)	-8074(3)	-3837(2)	33(2)
$C_{(19')}$	-9286(4)	-9454(2)	-1102(2)	24(2)
$C_{(20')}$	-10905(4)	-9481(3)	-825(2)	38(2)
$C_{(21')}$	-7208(3)	-9924(2)	-1026(2)	26(2)
$C_{(22')}$	-6295(4)	-10177(3)	70(2)	44(2)

TABLE 2. Coordinates ($\times 10^3$) for Hydrogen Atoms in I

Atom	x	y	z	Atom	x	y	z
9-H^1	-206(3)	748(2)	-22(2)	9'-H^1	-268(4)	-745(3)	-44(2)
9-H^2	-231(4)	805(2)	38(2)	9'-H^2	-279(3)	-805(2)	8(2)
9-H^3	-157(4)	833(2)	-7(2)	9'-H^3	-336(4)	-722(2)	5(2)
11-H^1	-194(3)	408(2)	83(2)	11'-H^1	-231(4)	-1044(2)	-193(2)
11-H^2	-152(4)	401(2)	162(2)	11'-H^2	-320(4)	-1101(2)	-222(3)
11-H^3	-239(4)	456(3)	132(2)	11'-H^3	-268(3)	-1107(2)	-147(2)
12-H^1	247(3)	741(2)	343(2)	12'-H^1	-731(3)	-783(2)	-335(2)
12-H^2	166(4)	759(2)	281(2)	12'-H^2	-633(4)	-798(2)	-276(2)
12-H^3	176(4)	684(2)	320(2)	12'-H^3	-675(3)	-865(2)	-330(2)
14-H	409(3)	841(2)	312(2)	14'-H	-884(3)	-676(2)	-269(2)
15-H	517(3)	887(2)	415(2)	15'-H	-980(3)	-592(2)	-348(2)
16-H	597(3)	797(2)	498(2)	16'-H	-1071(3)	-641(2)	-448(2)
17-H	579(3)	665(2)	480(2)	17'-H	-1065(3)	-780(2)	-471(2)
18-H	470(3)	623(2)	378(2)	18'-H	-962(3)	-860(2)	-390(2)
20-H^1	557(4)	574(2)	42(2)	20'-H^1	-1155(4)	-931(3)	-99(2)
20-H^2	586(3)	507(2)	93(2)	20'-H^2	-1090(3)	-1002(3)	-75(2)
20-H^3	651(4)	585(3)	97(2)	20'-H3	-1050(4)	-925(2)	-40(2)
22-H^1	215(4)	454(2)	7(2)	22'-H^1	-588(4)	-1060(3)	-8(2)
22-H^2	186(4)	393(3)	52(2)	22'-H^2	-699(4)	-1042(2)	18(2)
22-H^3	95(4)	458(3)	25(2)	22'-H^3	-585(4)	-993(2)	43(2)

can also be expected from molecules of a saturated zwitterionic form with the positive charge on S_2 and negative charge on O_1. This also brings about a shortening of the S_2-C_3 bond to 1.736(4) and of C_2-C_8 to 1.483(6) when compared with the C_3-C_{10} bond (1.502(6) Å). A similar non-equivalence in the S−C (sp^2) and C−C bond lengths was reported in [9].

EXPERIMENTAL

2,3,4',5'-Tetracarbomethoxy-5-methyl-6-phenylthiopyran-4-spiro-2'-(1,3-dithiole) (I, $C_{22}H_{20}O_8S_3$). A solution of thione II (0.01 mole) and ester III (0.02 mole) in benzene (5 ml) was refluxed for 8 h, evaporated, and crystallized from hexane-ethyl acetate to give product (73%) as light yellow crystals with mp 153-154°C.

X-Ray Structural Investigation. Crystals of I were monoclinic. At −120°C, a = 13.303(3), b = 17.119(4), c = 20.451(6) Å, β = 103.49(2)°, Z = 8, space group $P2_{1/c}$. Cell parameters and intensities of 5661 independent reflections were measured on a Siemens P3/PC diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$ scanning, $\theta \leq 25°$). 4301 reflections

TABLE 3. Bond Lengths d (Å) in the Nonequivalent Molecules I and I′

Bond	d		Bond	d	
	I	I′		I	I′
$S_{(1)}—C_{(1)}$	1,868(4)	1,884(4)	$C_{(1)}—C_{(4)}$	1,535(5)	1,530(5)
$S_{(1)}—C_{(2)}$	1,757(4)	1,750(5)	$C_{(1)}—C_{(7)}$	1,514(6)	1,506(6)
$S_{(2)}—C_{(1)}$	1,879(4)	1,869(4)	$C_{(2)}—C_{(3)}$	1,337(5)	1,340(5)
$S_{(2)}—C_{(3)}$	1,733(4)	1,739(4)	$C_{(2)}—C_{(8)}$	1,481(6)	1,485(6)
$S_{(3)}—C_{(5)}$	1,737(5)	1,749(5)	$C_{(3)}—C_{(10)}$	1,506(6)	1,497(6)
$S_{(3)}—C_{(6)}$	1,740(4)	1,745(4)	$C_{(4)}—C_{(5)}$	1,326(6)	1,321(6)
$O_{(1)}—C_{(8)}$	1,196(6)	1,197(6)	$C_{(4)}—C_{(12)}$	1,510(7)	1,499(7)
$O_{(2)}—C_{(8)}$	1,341(5)	1,336(5)	$C_{(5)}—C_{(13)}$	1,502(5)	1,494(5)
$O_{(2)}—C_{(9)}$	1,452(5)	1,453(5)	$C_{(6)}—C_{(7)}$	1,330(7)	1,329(6)
$O_{(3)}—C_{(10)}$	1,191(7)	1,200(6)	$C_{(6)}—C_{(19)}$	1,494(6)	1,505(6)
$O_{(4)}—C_{(10)}$	1,314(5)	1,328(4)	$C_{(7)}—C_{(21)}$	1,523(5)	1,523(5)
$O_{(4)}—C_{(11)}$	1,454(6)	1,446(7)	$C_{(13)}—C_{(14)}$	1,385(5)	1,384(5)
$O_{(5)}—C_{(19)}$	1,197(5)	1,204(4)	$C_{(13)}—C_{(18)}$	1,383(5)	1,397(5)
$O_{(6)}—C_{(19)}$	1,320(6)	1,314(6)	$C_{(14)}—C_{(15)}$	1,383(6)	1,376(6)
$O_{(6)}—C_{(20)}$	1,440(7)	1,450(7)	$C_{(15)}—C_{(16)}$	1,371(6)	1,369(6)
$O_{(7)}—C_{(21)}$	1,190(5)	1,194(5)	$C_{(16)}—C_{(17)}$	1,372(6)	1,382(7)
$O_{(8)}—C_{(21)}$	1,328(5)	1,329(4)	$C_{(17)}—C_{(18)}$	1,382(5)	1,376(6)
$O_{(8)}—C_{(22)}$	1,457(6)	1,448(5)			

TABLE 4. Valence Angles (deg) in the Nonequivalent Molecules I and I′

Angle	I	I′	Angle	I	I′
$C_{(1)}—S_{(1)}—C_{(2)}$	97,3(2)	97,6(2)	$S_{(3)}—C_{(6)}—C_{(19)}$	112,8(3)	112,1(3)
$C_{(1)}—S_{(2)}—C_{(3)}$	97,9(2)	98,1(2)	$C_{(7)}—C_{(6)}—C_{(19)}$	121,7(3)	121,9(3)
$C_{(5)}—S_{(3)}—C_{(6)}$	101,6(2)	101,0(2)	$C_{(1)}—C_{(7)}—C_{(6)}$	126,0(3)	125,2(3)
$C_{(8)}—O_{(2)}—C_{(9)}$	115,3(3)	116,7(4)	$C_{(1)}—C_{(7)}—C_{(21)}$	114,7(4)	116,7(4)
$C_{(10)}—O_{(4)}—C_{(11)}$	115,0(4)	115,4(4)	$C_{(6)}—C_{(7)}—C_{(21)}$	119,3(4)	118,0(4)
$C_{(19)}—O_{(6)}—C_{(20)}$	118,0(3)	116,6(3)	$O_{(1)}—C_{(8)}—O_{(2)}$	123,9(4)	125,7(4)
$C_{(21)}—O_{(8)}—C_{(22)}$	114,1(3)	113,8(3)	$O_{(1)}—C_{(8)}—C_{(2)}$	124,6(4)	123,9(4)
$S_{(1)}—C_{(1)}—S_{(2)}$	106,5(2)	106,3(2)	$O_{(2)}—C_{(8)}—C_{(2)}$	111,4(4)	110,3(4)
$S_{(1)}—C_{(1)}—C_{(4)}$	109,2(2)	107,8(2)	$O_{(3)}—C_{(10)}—O_{(4)}$	124,8(4)	124,4(4)
$S_{(2)}—C_{(1)}—C_{(4)}$	107,5(3)	110,0(3)	$O_{(3)}—C_{(10)}—C_{(3)}$	123,6(4)	123,8(3)
$S_{(1)}—C_{(1)}—C_{(7)}$	109,6(2)	107,6(2)	$O_{(4)}—C_{(10)}—C_{(3)}$	111,4(4)	111,6(4)
$S_{(2)}—C_{(1)}—C_{(7)}$	108,4(2)	108,8(2)	$C_{(5)}—C_{(13)}—C_{(4)}$	122,1(3)	119,3(3)
$C_{(4)}—C_{(1)}—C_{(7)}$.	115,3(3)	115,9(3)	$C_{(5)}—C_{(13)}—C_{(18)}$	118,8(3)	121,2(3)
$S_{(1)}—C_{(2)}—C_{(3)}$	118,5(3)	118,3(3)	$C_{(14)}—C_{(13)}—C_{(18)}$	119,0(3)	119,2(3)
$S_{(1)}—C_{(2)}—C_{(8)}$	119,4(3)	119,2(3)	$C_{(13)}—C_{(14)}—C_{(15)}$	119,6(4)	120,5(3)
$C_{(3)}—C_{(2)}—C_{(8)}$	122,1(4)	122,4(4)	$C_{(14)}—C_{(15)}—C_{(16)}$	120,8(4)	120,2(4)
$S_{(2)}—C_{(3)}—C_{(2)}$	118,5(3)	118,7(4)	$C_{(15)}—C_{(16)}—C_{(17)}$	120,0(4)	120,0(4)
$S_{(2)}—C_{(3)}—C_{(10)}$	114,1(3)	114,1(3)	$C_{(16)}—C_{(17)}—C_{(18)}$	119,6(4)	120,5(4)
$C_{(2)}—C_{(3)}—C_{(10)}$	127,2(4)	127,2(4)	$C_{(13)}—C_{(18)}—C_{(17)}$	121,0(4)	119,6(4)
$C_{(1)}—C_{(4)}—C_{(5)}$	123,7(4)	123,4(4)	$O_{(5)}—C_{(19)}—O_{(6)}$	123,4(5)	124,6(4)
$C_{(1)}—C_{(4)}—C_{(12)}$	114,3(4)	115,0(4)	$O_{(5)}—C_{(19)}—C_{(6)}$	125,2(4)	123,9(4)
$C_{(5)}—C_{(4)}—C_{(12)}$	122,0(3)	121,6(3)	$O_{(6)}—C_{(19)}—C_{(6)}$	111,3(3)	111,6(3)
$S_{(3)}—C_{(5)}—C_{(4)}$	127,4(3)	127,6(3)	$O_{(7)}—C_{(21)}—O_{(8)}$	125,1(3)	124,6(3)
$S_{(3)}—C_{(5)}—C_{(13)}$	108,6(3)	106,7(3)	$O_{(7)}—C_{(21)}—C_{(7)}$	124,6(3)	122,6(3)
$C_{(4)}—C_{(5)}—C_{(13)}$	123,9(4)	125,6(4)	$O_{(8)}—C_{(21)}—C_{(7)}$	110,3(3)	112,8(3)
$S_{(3)}—C_{(6)}—C_{(7)}$	125,5(3)	126,0(3)			

with $I \geq 2\sigma(I)$ were used for solution and refinement of the structure. It was solved by a direct method and refined by full matrix least squares analysis in the anisotropic approximation for all non-hydrogen atoms. The directly revealed hydrogen atoms were refined to $B_{iso} = 5$ Å^2. The final difference factors were $R = 0.044$ and $R_W = 0.043$. All calculations were on an IBM PC/AT computer using the SHELX PLUS program [10]. Coordinates of non-hydrogen atoms are given in Table 1, coordinates of hydrogen atoms in Table 2, and bond lengths and valence angles in Tables 3 and 4 respectively.

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