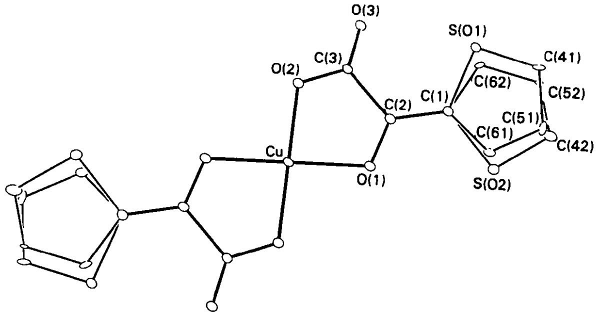

Fig. 1. $[Cu(C_6H_3O_3S)_2]$. Vue de la molécule avec les deux positions des cycles thiényle-2. La probabilité des ellipsoïdes est de 5%.

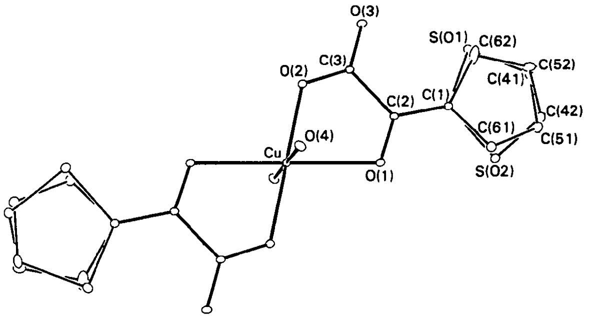

Fig. 2. $[Cu(C_6H_3O_3S)_2(H_2O)_2]$. Vue de la molécule avec les deux positions des cycles thiényle-2. La probabilité des ellipsoïdes est de 5%.

grande dans le complexe hydraté [2,290 (2) dans (2) au lieu de 1,965 (4) Å dans (1)]. Cela se traduit aussi par une diminution de l'angle O(1)—Cu—O(2) [76,52 (5) dans (2) au lieu de 83,8 (1)° dans (1)].

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Structures of Three Thiochromone Photodimers

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Abstract. 4*H*-Benzo[1]thiin-4-one dimers with different ring fusions, 5a,5b,11a,11b-tetrahydro-11*H*,12*H*-dibenzo[1,2-*e*:1′,2′-*e*′]cyclobuta[1,2-*b*:4,3-*b*′]dithiin-11,12-dione, $C_{18}H_{12}O_2S_2$. Room temperature. Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7093$ Å. $M_r = 324$. Dimer (3): monoclinic, $P2_1/a$, $a = 11{\cdot}614\,(2)$, $b = 15{\cdot}614\,(2)$, $c = 16{\cdot}210\,(2)$ Å, $\beta = 90{\cdot}02\,(1)°$, $V = 2939{\cdot}8$ Å^3, $Z = 8$, $D_x = 1{\cdot}466$ Mg m^{-3}, μ(Mo $K\alpha$) = $0{\cdot}35$ mm^{-1}, $F(000) = 1344$, $R_F = 0{\cdot}076$, $wR_F = 0{\cdot}039$ for 2023 reflections. Dimer (4): triclinic, $P\bar{1}$, $a = 5{\cdot}692\,(2)$, $b = 11{\cdot}404\,(7)$, $c = 11{\cdot}759\,(4)$ Å, $\alpha = 74{\cdot}40\,(4)$, $\beta = 89{\cdot}78\,(3)$, $\gamma = 75{\cdot}69\,(3)°$, $V = 711{\cdot}3$ Å^3, $Z = 2$, $D_x = 1{\cdot}515$ Mg m^{-3}, μ(Mo $K\alpha$) = $0{\cdot}36$ mm^{-1}, $F(000) = 336$, $R_F = 0{\cdot}064$, $wR_F = 0{\cdot}032$ for 1735 reflections. Dimer (5): monoclinic, $P2/c$, $a = 8{\cdot}389\,(1)$, $b = 9{\cdot}657\,(1)$, $c = 9{\cdot}573\,(1)$ Å, $\beta = 112{\cdot}064\,(9)°$, $V = 718{\cdot}7$ Å^3, $Z = 2$, $D_x = 1{\cdot}499$ Mg m^{-3}, μ(Mo $K\alpha$) = $0{\cdot}36$ mm^{-1}, $F(000) = 336$, $R_F = 0{\cdot}064$, $wR_F = 0{\cdot}030$ for 880 reflections. All three dimers are of cyclobutane {2 + 2} type. Dimers (3, II) and (5, IV) are head-to-head (*HH*, sulfur atoms on same side of molecule), dimer (3) being fused *anti* at the cyclobutane ring and dimer (5) being *cis,trans*. Dimer (4, III) has *syn* fusion but, because of disorder in the crystal, cannot be unambiguously assigned as either *HH* or head-to-tail, *HT*. The infrared spectrum supports the *HH* structure.

Introduction. Photodimerization of thiochromone (I) was first reported by Still & Leong (1981). Four photodimers, (2) through (5), were identified as being of cyclobutane {2 + 2} type and a specific stereochemistry was assigned to each on the basis of ^{1}H NMR, ^{13}C NMR and IR data. Crystals suitable for X-ray analysis were obtained from dimers (3), (4) and (5). The results show that none of the original stereochemical assignments was correct.

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† Deceased.

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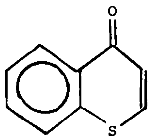


(I)

Experimental. The dimers were prepared by photolysis of thiochromone (I) in benzene. Dimer (3) was recrystallized from dichloromethane/hexane, (4) and (5) from acetone. Details are given in Still & Leong (1981).

X-ray diffraction data collected on automated four-circle Picker diffractometer with Zr-filtered Mo $K\alpha$ radiation in θ–2θ scan mode with profile analysis (Grant & Gabe, 1978). Intensities not corrected for absorption. Other experimental details are set out in Table 1. Three structures solved using *MULTAN* (Germain, Main & Woolfson, 1971), dimers (3) and (4) refined on F by block-diagonal least squares and dimer (5) by full-matrix least squares with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms given positions based on positions of atoms to which they were attached and given isotropic B_{eq} values of these atoms. $w = 1/\sigma^2(F)$ with $\sigma(F)$ based on counting statistics. Scattering factors from *International Tables for X-ray Crystallography* (1974). Crystals of dimer (3) were the weakest X-ray scatterers of the three (see 2θ range, Table 1) and this might account for the somewhat higher R_F of 0·076. NRC PDP-8e system of programs used in all calculations (Larson & Gabe, 1978).*

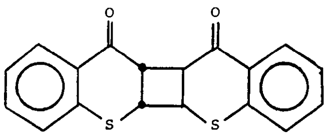
Table 1. *Experimental data*

	Dimer (3)	Dimer (4)	Dimer (5)
Crystal dimensions (mm)	0·35 × 0·2 × 0·15	0·3 × 0·2 × 0·2	0·3 × 0·2 × 0·25
Number of reflections for lattice parameters and their 2θ range (°)	46 $35 < 2\theta < 40$	22 $40 < 2\theta < 50$	42 $40 < 2\theta < 45$
$2\theta_{max}$(°)	50	55	50
Max. values of $\|h\|,\|k\|,\|l\|$ scanned	14,19,20	8,15,16	10,12,12
Standard reflections (and % variation)	400, 060, 002 (3%)	200, 040, 016 (2%)	310, 030, 002 (1%)
Number of measured reflections	5518	3564	1646
Number of unique reflections	5192	3264	1269
R_{int}	0·04	0·01	0·01
Number of significant reflections [$I > 2{\cdot}5\sigma(I)$]	2023	1735	880
R_F	0·076	0·064	0·056
wR_F	0·039	0·032	0·026
S	3·6	4·9	4·6
$\Delta\rho_{max}$(e Å^{-3})	0·39	0·37	0·33
$(\Delta/\sigma)_{max}$	0·2	0·4	0·50
Secondary extinction (μm)	—	—	0·0051

The atomic positional and equivalent isotropic temperature factors for the non-hydrogen atoms are given for the three dimers in Tables 2, 3 and 4.

Discussion. Of the four dimers, (2) through (5), obtained from thiochromone (I), dimer (2) could not be obtained as crystals suitable for X-ray structure analysis.

Photodimer (3). Although the unit cell has $\beta = 90°$, the Laue symmetry and systematic absences show the space group to be unambiguously $P2_1/a$ with two independent molecules, A and B, per asymmetric unit. The two molecules are illustrated in Fig. 1(*a*), (*b*) and by formula (II). Bond lengths and interbond angles are given in Tables 5 and 6.



(II)

Table 2. *Atomic coordinates and B_{eq} values for non-hydrogen atoms of dimer* (3)

	x	y	z	B_{eq}(Å^2)*
S(*A*)	0·3982 (2)	0·2614 (2)	0·2667 (2)	4·3 (2)
S(*A*′)	0·1673 (2)	0·4393 (2)	0·3377 (2)	5·2 (2)
O(*A*)	0·6235 (5)	0·3391 (4)	0·4639 (3)	6·7 (6)
O(*A*′)	0·3370 (5)	0·4401 (5)	0·5773 (4)	8·9 (7)
C(*A*2)	0·3422 (7)	0·3119 (6)	0·3583 (5)	3·8 (6)
C(*A*3)	0·4256 (7)	0·3325 (5)	0·4309 (5)	3·4 (6)
C(*A*4)	0·5521 (7)	0·3397 (6)	0·4087 (5)	4·2 (7)
C(*A*5)	0·6910 (7)	0·3958 (6)	0·3083 (5)	3·8 (6)
C(*A*6)	0·7303 (7)	0·4082 (5)	0·2281 (5)	3·8 (6)
C(*A*7)	0·6657 (7)	0·3733 (6)	0·1635 (5)	4·9 (7)
C(*A*8)	0·5662 (7)	0·3357 (5)	0·1761 (5)	3·5 (6)
C(*A*9)	0·5257 (7)	0·3213 (5)	0·2557 (5)	3·5 (6)
C(*A*10)	0·5894 (7)	0·3525 (5)	0·3224 (5)	3·4 (6)
C(*A*2′)	0·3146 (6)	0·4065 (5)	0·3510 (4)	3·0 (6)
C(*A*3′)	0·3690 (7)	0·4227 (5)	0·4361 (5)	3·4 (6)
C(*A*4′)	0·2955 (7)	0·4270 (6)	0·5113 (5)	4·9 (7)
C(*A*5′)	0·1109 (8)	0·3847 (6)	0·5772 (5)	5·2 (6)
C(*A*6′)	−0·0042 (8)	0·3711 (6)	0·5792 (5)	6·2 (7)
C(*A*7′)	−0·0649 (7)	0·3787 (6)	0·5076 (6)	6·1 (8)
C(*A*8′)	−0·0135 (7)	0·3954 (6)	0·4358 (5)	5·1 (7)
C(*A*9′)	0·1038 (7)	0·4098 (6)	0·4322 (5)	4·1 (6)
C(*A*10′)	0·1687 (7)	0·4043 (6)	0·5056 (5)	4·1 (6)
S(*B*)	1·0701 (2)	0·4068 (2)	0·8414 (2)	5·2 (2)
S(*B*′)	0·8228 (2)	0·2475 (2)	0·7682 (2)	4·1 (2)
O(*B*)	0·9250 (5)	0·3376 (5)	1·0850 (3)	6·4 (6)
O(*B*′)	0·6092 (5)	0·3536 (4)	0·9647 (3)	6·0 (6)
C(*B*2)	0·9219 (6)	0·3812 (5)	0·8655 (5)	3·2 (6)
C(*B*3)	0·8784 (7)	0·3902 (5)	0·9536 (5)	2·7 (5)
C(*B*4)	0·9602 (7)	0·3663 (5)	1·0248 (5)	3·5 (6)
C(*B*5)	1·1524 (7)	0·3780 (6)	1·0849 (5)	4·1 (6)
C(*B*6)	1·2696 (8)	0·3949 (6)	1·0799 (5)	5·4 (7)
C(*B*7)	1·3200 (6)	0·4124 (6)	1·0052 (5)	5·0 (7)
C(*B*8)	1·2575 (7)	0·4141 (6)	0·9347 (5)	3·9 (6)
C(*B*9)	1·1390 (7)	0·3976 (5)	0·9390 (5)	3·7 (6)
C(*B*10)	1·0864 (6)	0·3822 (5)	1·0127 (5)	3·0 (5)
C(*B*2′)	0·8794 (6)	0·2900 (5)	0·8632 (5)	3·4 (6)
C(*B*3′)	0·7979 (6)	0·3095 (5)	0·9342 (4)	3·1 (6)
C(*B*4′)	0·6765 (7)	0·3425 (6)	0·9117 (5)	3·9 (6)
C(*B*5′)	0·5517 (7)	0·4049 (6)	0·8073 (5)	3·8 (6)
C(*B*6′)	0·5100 (7)	0·4171 (6)	0·7281 (5)	4·4 (7)
C(*B*7′)	0·5628 (7)	0·3760 (5)	0·6638 (5)	4·0 (6)
C(*B*8′)	0·6594 (7)	0·3253 (6)	0·6779 (5)	4·4 (7)
C(*B*9′)	0·7030 (7)	0·3154 (5)	0·7568 (5)	3·5 (6)
C(*B*10′)	0·6464 (6)	0·3549 (5)	0·8227 (5)	3·1 (6)

* In this table, and in Tables 3 and 4, $B_{eq} = \frac{8}{3}\pi^2 \sum_i U_{ii}$.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42774 (73 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

As will be seen, both molecules are of *HH* type (sulfur atoms on the same side of the molecule) and fused *anti* at the cyclobutane ring (two heterocyclic ring bonds up and two down with respect to the mean cyclobutane plane; see Table 7*a*). The heterocyclic rings themselves have differing conformations, Table 7(*b*). Where both the sulfur atom and the keto group are on the same side of the central heterocyclic ring mean plane, the conformation is that of a boat; where they are on opposite sides, the conformation is that of a chair. In those cases where the keto group lies within

Table 3. *Atomic coordinates and* B_{eq} *values for non-hydrogen atoms of dimer* (4)

Keto carbon atoms were constrained. Atomic sites marked by asterisks are half-occupied.

	x	y	z	B_{eq}(Å^2)
S(11)*	0·2840 (3)	0·9513 (2)	0·6261 (2)	4·2 (1)
S(11′)*	0·5693 (4)	0·7705 (2)	0·9139 (2)	5·4 (2)
O(11)*	0·6051 (8)	0·7675 (4)	0·9869 (4)	4·9 (3)
O(11′)*	0·1633 (8)	0·9954 (4)	0·5833 (4)	4·9 (3)
C(12)	0·5637 (6)	0·9546 (4)	0·6801 (3)	5·0 (3)
C(13)	0·6342 (6)	0·9102 (4)	0·8145 (3)	5·6 (3)
C(14)*	0·5427	0·8020	0·8885	13·8 (12)
C(14′)*	0·3189	0·9249	0·6528	7·0 (6)
C(15)	0·2998 (7)	0·6351 (4)	0·8970 (3)	5·5 (3)
C(16)	0·1491 (8)	0·5838 (4)	0·8460 (3)	7·4 (4)
C(17)	0·0554 (8)	0·6401 (4)	0·7307 (3)	7·1 (3)
C(18)	0·1157 (6)	0·7478 (3)	0·6672 (3)	4·8 (2)
C(19)	0·2668 (6)	0·8019 (3)	0·7177 (3)	3·7 (2)
C(110)	0·3626 (6)	0·7424 (3)	0·8339 (3)	4·5 (2)
S(21)*	0·3398 (4)	1·2273 (2)	0·5849 (2)	5·3 (2)
S(21′)*	0·2411 (4)	1·0472 (2)	0·8741 (2)	4·7 (1)
O(21)*	0·1550 (8)	1·0057 (4)	0·9174 (4)	4·7 (3)
O(21′)*	0·3835 (9)	1·2319 (5)	0·5118 (4)	5·8 (4)
C(22)	0·5471 (6)	1·0895 (4)	0·6850 (3)	5·5 (3)
C(23)	0·5173 (6)	1·0452 (4)	0·8189 (3)	5·9 (3)
C(24)*	0·2429	1·0752	0·8471	8·2 (6)
C(24′)*	0·3513	1·1975	0·6109	15·6 (12)
C(25)	−0·1336 (7)	1·2506 (3)	0·8334 (3)	4·9 (2)
C(26)	−0·3021 (7)	1·3574 (4)	0·7701 (3)	6·4 (3)
C(27)	−0·2651 (8)	1·4148 (4)	0·6535 (3)	7·0 (3)
C(28)	−0·0625 (8)	1·3642 (4)	0·6029 (3)	6·7 (3)
C(29)	0·1100 (7)	1·2567 (4)	0·6658 (3)	5·3 (2)
C(210)	0·0690 (6)	1·1973 (3)	0·7825 (3)	4·5 (2)

Table 4. *Atomic coordinates and* B_{eq} *values for non-hydrogen atoms of dimer* (5)

All atomic sites are half-occupied.

	x	y	z	B_{eq}(Å^2)
S	0·4873 (2)	0·4637 (1)	0·3059 (1)	3·74 (8)
O	0·3298 (5)	0·7265 (3)	−0·0841 (4)	4·6 (2)
C(2)	0·4561 (10)	0·6427 (5)	0·3197 (6)	2·4 (3)
C(3)	0·4192 (18)	0·7316 (18)	0·1770 (13)	5·1 (9)
C(4)	0·3378 (8)	0·6627 (6)	0·0244 (7)	2·9 (3)
C(5)	0·1256 (6)	0·4871 (5)	−0·1174 (5)	3·1 (2)
C(6)	0·0492 (6)	0·3595 (5)	−0·1330 (5)	3·5 (3)
C(7)	0·1095 (14)	0·2624 (9)	−0·0174 (8)	4·1 (5)
C(8)	0·2437 (7)	0·2988 (5)	0·1164 (5)	3·7 (3)
C(9)	0·3175 (6)	0·4290 (4)	0·1344 (5)	2·7 (2)
C(10)	0·2603 (6)	0·5227 (5)	0·0152 (5)	2·4 (2)
S′	0·8148 (2)	0·6686 (1)	0·5101 (1)	3·96 (9)
O′	0·6422 (4)	0·9915 (3)	0·1487 (4)	5·0 (2)
C(2′)	0·6149 (12)	0·7347 (14)	0·3944 (10)	2·9 (5)
C(3′)	0·5935 (14)	0·7624 (14)	0·2293 (13)	8·9 (12)
C(4′)	0·6986 (7)	0·8965 (5)	0·2334 (6)	3·5 (3)
C(5′)	0·9981 (8)	0·9789 (4)	0·3177 (5)	3·7 (3)
C(6′)	1·1713 (7)	0·9707 (5)	0·4059 (6)	4·4 (3)
C(7′)	1·2287 (7)	0·8733 (6)	0·5207 (6)	4·3 (3)
C(8′)	1·1166 (14)	0·7842 (11)	0·5484 (9)	4·0 (5)
C(9′)	0·9403 (7)	0·7908 (5)	0·4601 (5)	3·2 (3)
C(10′)	0·8812 (6)	0·8890 (5)	0·3434 (5)	2·8 (2)

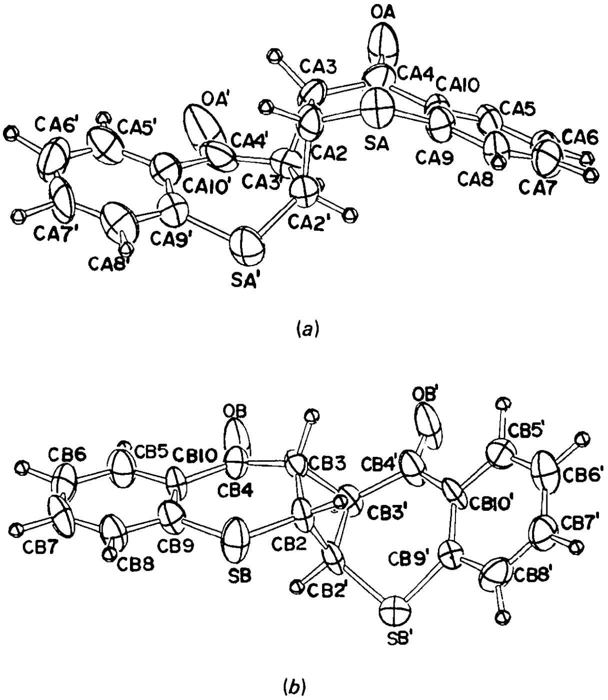


Fig. 1 (*a*) *ORTEP* plot (Johnson, 1965), of molecule *A* of dimer (3) with 50% probability ellipsoids. (Hydrogen atoms have fictitious $B = 0{\cdot}8$ Å^2.) (*b*) *ORTEP* plot of molecule *B* of dimer (3).

Table 5. *Bond lengths* (Å)

The larger standard deviations in the bond lengths of dimer (3) could possibly be due to the poor diffracting power of the crystals.

Dimer	(3*A*)	(3*B*)	(5)	(4)	
S–C(2)	1·803 (9)	1·811 (8)	1·762 (5)	S(11)–C(12)	1·730 (4)
				S(11′)–C(13)	1·824 (5)
S′–C(2′)	1·799 (8)	1·802 (8)	1·747 (11)	S(21)–C(22)	1·830 (5)
				S(21′)–C(23)	1·697 (4)
S–C(9)	1·762 (9)	1·779 (8)	1·754 (5)	S(11)–C(19)	1·780 (4)
				S(11′)–C(110)	1·652 (4)
S′–C(9′)	1·762 (9)	1·760 (8)	1·763 (6)	S(21)–C(29)	1·636 (4)
				S(21′)–C(210)	1·800 (4)
C(2)–C(3)	1·557 (10)	1·522 (11)	1·548 (12)	C(12)–C(13)	1·546 (5)
C(2′)–C(3′)	1·537 (10)	1·521 (11)	1·533 (15)	C(22)–C(23)	1·541 (5)
C(2)–C(2′)	1·515 (12)	1·507 (11)	1·543 (12)	C(12)–C(22)	1·534 (6)
C(3)–C(3′)	1·557 (11)	1·599 (10)	1·387 (17)	C(13)–C(23)	1·534 (6)
C(3)–C(4)	1·516 (12)	1·540 (10)	1·496 (16)	C(13)–C(14)	1·513
				C(12′)–C(14′)	1·568
C(3′)–C(4′)	1·490 (12)	1·545 (11)	1·541 (13)	C(23)–C(24)	1·569
				C(22)–C(24′)	1·507
C(4)–O	1·220 (9)	1·149 (10)	1·187 (7)	C(14)–O(11)	1·144
				C(14′)–O(11′)	1·183
C(4′) O′	1·192 (10)	1·175 (10)	1·198 (7)	C(24)–O(21)	1·185
				C(24′)–O(21′)	1·156
C(4)–C(10)	1·478 (11)	1·500 (10)	1·487 (8)	C(14)–C(110)	1·584
				C(14′)–C(19)	1·505
C(4′)–C(10′)	1·518 (11)	1·497 (10)	1·497 (7)	C(24)–C(210)	1·500
				C(24′)–C(29)	1·590
C(5)–C(6)	1·392 (11)	1·388 (12)	1·371 (8)	C(15)–C(16)	1·370 (6)
C(5′)–C(6′)	1·354 (12)	1·385 (11)	1·382 (8)	C(25)–C(26)	1·378 (5)
C(5)–C(10)	1·379 (11)	1·401 (10)	1·388 (6)	C(15)–C(110)	1·379 (6)
C(5′)–C(10′)	1·375 (12)	1·372 (11)	1·400 (8)	C(25)–C(210)	1·379 (5)
C(6)–C(7)	1·398 (11)	1·373 (12)	1·392 (10)	C(16)–C(17)	1·379 (6)
C(6′)–C(7′)	1·362 (12)	1·370 (12)	1·388 (9)	C(26)–C(27)	1·391 (6)
C(7)–C(8)	1·312 (12)	1·353 (11)	1·396 (11)	C(17)–C(18)	1·378 (6)
C(7′)–C(8′)	1·334 (12)	1·391 (12)	1·372 (13)	C(27)–C(28)	1·368 (6)
C(8)–C(9)	1·391 (11)	1·402 (11)	1·384 (8)	C(18)–C(19)	1·393 (5)
C(8′)–C(9′)	1·383 (11)	1·384 (11)	1·403 (12)	C(28)–C(29)	1·392 (6)
C(9)–C(10)	1·398 (10)	1·363 (11)	1·393 (7)	C(19)–C(110)	1·396 (5)
C(9′)–C(10′)	1·411 (11)	1·398 (11)	1·406 (7)	C(29)–C(210)	1·404 (5)

±0·05 Å of the central mean plane, we have designated the conformation as that of a sofa. It will be seen that, in dimer (3), molecule *A* has two boat rings while molecule *B* has one boat ring and one chair ring.

Photodimer (4). The best *MULTAN* solution, Fig. 2, shows that the molecular image consists of two superimposed *syn* molecules (both heterocyclic rings on the same side of the mean cyclobutane plane), one of which has been rotated 180° with respect to the other about an axis through the center of the cyclobutane ring, normal to its mean plane. On the basis of electron density and effective anisotropic temperature factors in the cyclobutane ring and the outer benzene rings, the geometrical superposition of these rings is extremely close. Unconstrained least-squares refinement of the other atoms was not possible, however, because of the closeness of the half-occupied sulfur positions S(11), S(11′), S(21) and S(21′) to the half-occupied carbon positions C(14′), C(14), C(24) and C(24′) (see Fig. 2). It is not possible to infer whether these disordered positions arise from the superposition of *HH* or of *HT* dimers. [For reasons given below, the *HH* stereoisomer has been assumed in space formula (III)]. A planar idealized model of the keto group plus two attached

Table 6. *Interbond angles* (°)

Dimer	(3*A*)	(3*B*)	(5)	(4)	
C(2)–S–C(9)	98·9 (4)	102·6 (4)	99·3 (3)	C(12)–S(11)–C(19)	99·0 (2)
				C(13)–S(11′)–C(110)	102·2 (2)
C(2′)–S′–C(9′)	102·7 (4)	98·9 (4)	96·6 (5)	C(22)–S(21)–C(29)	102·4 (2)
				C(23)–S(21′)–C(210)	99·6 (2)
S–C(2)–C(3)	119·2 (6)	119·9 (5)	116·6 (9)	S(11)–C(12)–C(13)	120·8 (3)
				S(11′)–C(13)–C(12)	123·5 (3)
S′–C(2′)–C(3′)	116·8 (6)	119·6 (5)	115·1 (8)	S(21)–C(22)–C(23)	123·3 (3)
				S(21′)–C(23)–C(22)	122·0 (3)
S–C(2)–C(2′)	116·0 (6)	121·0 (6)	117·7 (7)	S(11)–C(12)–C(22)	107·8 (3)
				S(11′)–C(13)–C(23)	124·1 (3)
S′–C(2′)–C(2)	119·2 (6)	119·2 (6)	123·2 (9)	S(21)–C(22)–C(12)	122·6 (2)
				S(21′)–C(23)–C(13)	107·4 (3)
C(3)–C(2)–C(2′)	89·4 (6)	90·1 (6)	86·4 (7)	C(13)–C(12)–C(22)	88·0 (3)
C(3′)–C(2′)–C(2)	90·2 (6)	89·8 (6)	83·7 (7)	C(23)–C(22)–C(12)	88·1 (3)
C(2)–C(3)–C(4)	116·0 (7)	118·4 (6)	120·5 (5)	C(12)–C(13)–C(14)	117·7
				C(13)–C(12)–C(14′)	110·9
C(2′)–C(3′)–C(4′)	120·4 (7)	117·1 (6)	107·4 (10)	C(22)–C(23)–C(24)	111·5
				C(23)–C(22)–C(24′)	117·8
C(2)–C(3)–C(3′)	88·0 (6)	86·4 (6)	88·6 (7)	C(12)–C(13)–C(23)	87·9 (3)
C(2′)–C(3′)–C(3)	88·6 (6)	86·7 (6)	92·7 (9)	C(22)–C(23)–C(13)	88·2 (3)
C(4)–C(3)–C(3′)	110·8 (7)	108·5 (6)	121·6 (18)	C(14)–C(13)–C(23)	120·1
				C(14′)–C(12)–C(22)	116·4
C(4′)–C(3′)–C(3)	109·1 (7)	108·5 (6)	135·2 (11)	C(24)–C(23)–C(13)	116·5
				C(24′)–C(22)–C(12)	120·0
C(3)–C(4)–O	119·0 (7)	120·8 (7)	118·1 (7)	C(13)–C(14)–O(11)	116·5
				C(12)–C(14′)–O(11′)	123·8
C(3′)–C(4′)–O′	120·7 (8)	118·9 (7)	123·3 (6)	C(23)–C(24)–O(21)	124·3
				C(22)–C(24′)–O(21′)	116·2
C(3)–C(4)–C(10)	121·3 (6)	117·7 (7)	119·1 (7)	C(13)–C(14)–C(110)	121·9
				C(12)–C(14′)–C(19)	120·6
C(3′)–C(4′)–C(10′)	119·8 (7)	118·9 (7)	113·1 (5)	C(23)–C(24)–C(210)	120·9
				C(22)–C(24′)–C(29)	121·6
C(10)–C(4)–O	119·7 (7)	121·6 (7)	122·7 (6)	C(110)–C(14)–O(11)	121·6
				C(19)–C(14′)–O(11′)	115·6
C(10′)–C(4′)–O′	119·1 (8)	122·1 (7)	123·3 (4)	C(210)–C(24)–O(21)	114·5
				C(29)–C(24′)–O(21′)	122·2
C(6)–C(5)–C(10)	120·3 (7)	118·7 (8)	120·6 (5)	C(16)–C(15)–C(110)	120·8 (3)
C(6′)–C(5′)–C(10′)	122·5 (8)	121·8 (7)	120·2 (5)	C(26)–C(25)–C(210)	121·2 (3)
C(5)–C(6)–C(7)	117·9 (8)	120·4 (7)	120·2 (6)	C(15)–C(16)–C(17)	120·3 (4)
C(5′)–C(6′)–C(7′)	118·4 (8)	119·0 (7)	119·8 (5)	C(25)–C(26)–C(27)	119·7 (4)
C(6)–C(7)–C(8)	122·0 (8)	121·4 (7)	119·1 (8)	C(16)–C(17)–C(18)	119·4 (3)
C(6′)–C(7′)–C(8′)	122·0 (8)	120·2 (7)	121·3 (6)	C(26)–C(27)–C(28)	119·6 (4)
C(7)–C(8)–C(9)	121·0 (8)	118·7 (8)	120·8 (6)	C(17)–C(18)–C(19)	121·2 (3)
C(7′)–C(8′)–C(9′)	120·6 (8)	120·7 (8)	120·0 (9)	C(27)–C(28)–C(29)	121·5 (3)
S–C(9)–C(8)	117·7 (6)	112·5 (6)	117·2 (4)	S(11)–C(19)–C(18)	112·9 (3)
				S(11′)–C(110)–C(15)	109·1 (3)
S′–C(9′)–C(8′)	119·4 (6)	117·0 (7)	114·1 (6)	S(21)–C(29)–C(28)	109·6 (3)
				S(21)–C(210)–C(25)	113·6 (3)
S–C(9)–C(10)	123·5 (6)	126·3 (6)	123·5 (4)	S(11)–C(19)–C(110)	128·4 (3)
				S(11′)–C(110)–C(19)	130·9 (3)
S′–C(9′)–C(10′)	121·8 (6)	123·9 (6)	126·8 (4)	S(21)–C(29)–C(210)	131·7 (3)
				S(21′)–C(210)–C(29)	127·0 (3)
C(8)–C(9)–C(10)	118·8 (7)	121·1 (7)	119·2 (4)	C(18)–C(19)–C(110)	118·4 (3)
C(8′)–C(9′)–C(10′)	118·8 (8)	119·0 (7)	119·1 (6)	C(28)–C(29)–C(210)	118·7 (3)
C(4)–C(10)–C(5)	118·4 (7)	114·4 (7)	117·8 (5)	C(14)–C(110)–C(15)	122·3
				C(14′)–C(19)–C(18)	121·9
C(4′)–C(10′)–C(5′)	118·4 (7)	115·8 (7)	116·5 (5)	C(24)–C(210)–C(25)	121·8
				C(24′)–C(29)–C(28)	122·8
C(4)–C(10)–C(9)	122·0 (7)	125·7 (7)	122·2 (4)	C(14)–C(110)–C(19)	117·9
				C(14′)–C(19)–C(110)	119·7
C(4′)–C(10′)–C(9′)	123·7 (8)	124·7 (7)	123·5 (5)	C(24)–C(210)–C(29)	119·0
				C(24′)–C(29)–C(210)	118·7
C(5)–C(10)–C(9)	119·7 (7)	119·6 (7)	120·0 (5)	C(15)–C(110)–C(19)	119·9 (3)
C(5′)–C(10′)–C(9′)	117·8 (8)	119·3 (7)	119·8 (5)	C(25)–C(210)–C(29)	119·2 (3)

Table 7. *Displacement* (10^{-2} Å) *of atoms in heterocyclic rings from their central mean plane*

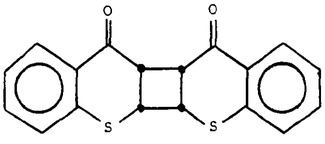
(*a*) Fusion of heterocyclic and cyclobutane rings

Dimer	Atoms defining plane				Other atoms; type of fusion at cyclobutane ring						Overall conformation
	C(2)	C(3)	C(2′)	C(3′)	S	C(4)		S′	C(4′)		
(3*A*)	−10	+10	+10	−10	+103	+149	*cis*	−99	−143	*cis*	*anti*
(3*B*)	+14	−13	−14	+13	−75	−157	*cis*	+80	+159	*cis*	*anti*
(5)	+15	−17	−15	+17	+176	+60	*cis*	+82	−43	*trans*	—
	C(12)	C(13)	C(22)	C(23)	S(11)	C(14)		S(21)	C(24)		
(4)	+11	−12	−17	+18	+173	+77	*cis*	+62	+170	*cis*	*syn*
					S(11′)	C(14′)		S(21′)	C(24′)		
					+72	+161	*cis*	+179	+65	*cis*	*syn*

(*b*) Conformations of heterocyclic rings

Dimer	Atoms defining plane				Other atoms			Conformation	Atoms defining plane				Other atoms			Conformation
	C(2)	C(3)	C(9)	C(10)	S	C(4)	O		C(2′)	C(3′)	C(9′)	C(10′)	S′	C(4′)	O′	
(3*A*)	+5	−6	−6	+6	−63	−24	−60	boat	−8	+8	−8	−9	+55	+16	+30	boat
(3*B*)	+9	−9	−10	+10	−25	+30	+72	chair	+9	−10	−10	+11	−59	−10	−32	boat
(5)	−6	+7	+7	−7	+68	+22	+49	boat	−21	+22	+24	−25	+54	−49	−109	chair
	C(12)	C(13)	C(19)	C(110)	S(11)	C(14)	O(11)	—	C(22)	C(23)	C(29)	C(210)	S(21)	C(24)	O(21)	—
(4)	+7	−7	−7	+7	−58	0	+5	sofa	+7	−7	−7	+7	−13	+41	+105	chair
					S(11′)	C(14′)	O(11)′)	—					S(21′)	C(24′)	O(21′)	—
					+18	−42	−11	chair					+56	0	+5	sofa

bonds was taken from dimer (3) and used to establish corresponding keto positions for the superimposed molecules of dimer (4) by the best-fitting program *BMFIT* (Yuen & Nyburg, 1979). The idealized geometry thus obtained was preserved throughout least-squares refinement. Even so some anisotropic thermal factors for these atoms were quite large. (See B_{eq} values in Table 3.) Because of the constraints, no estimates of the positional e.s.d.'s for the keto carbon atoms can be given. Each molecular image has one sofa and one chair heterocyclic ring, Table 7(*b*).



(III)

Notwithstanding the centric intensity statistics, an attempt was made to solve the structure in $P1$ but this was unsuccessful.

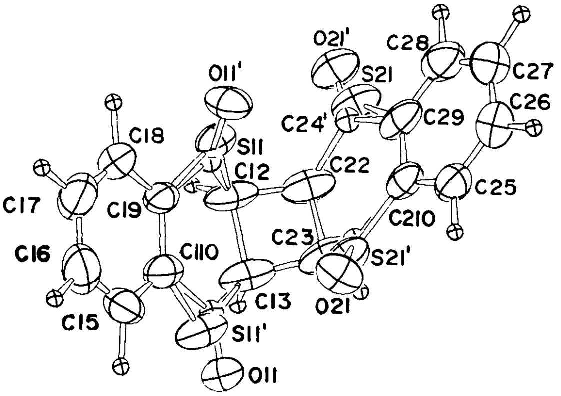


Fig. 2. *ORTEP* plot of dimer (4) showing two superimposed molecular images. [Disordered carbon atoms C(14), C(14′), C(24), C(24′) given fictitious $B = 1{\cdot}8$ Å^2.]

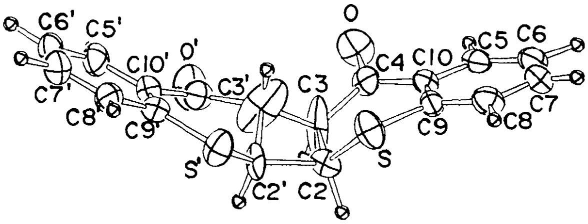
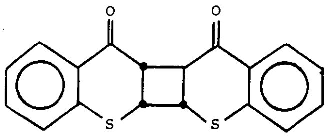


Fig. 3. *ORTEP* plot of dimer (5).

Photodimer (5). The only systematic reflection absences from this crystal corresponded to the presence of a *c* glide, whence the space group is either Pc or $P2/c$. Since $Z = 2$, a solution was attempted in Pc. No refinement of the best *MULTAN* solution could be effected. However, this showed four large independent peaks (instead of the expected two). These peaks were related in pairs about the diad axes. The origin was moved in the xz plane so that one diad axis lay at ($\frac{1}{2},y,\frac{1}{4}$) and the structure then refined in $P2/c$ with half-occupancies for all atoms. Initial block-diagonal-matrix least-squares refinement was uneventful but the refined anisotropic temperature factors of atoms C(3) and C(3′) were large. The structure was refined further by full-matrix least squares but this simply resulted in the bond lengths and interbond angles of chemically equivalent groups of atoms being in somewhat better accord than before; the anomalously large temperature factors of atoms C(3) and C(3′) remained (see Fig. 3). Atom C(3) lies close to atoms C(2′) (0·63 Å) and C(3′) (0·99 Å) of the other molecule image, but, if this has caused problems in refinement, it is difficult to see why the temperature factor of C(2′) is normal. It is possible that the cyclobutane is disordered with two buckled conformations hinged about C(2)–C(2′). We did not pursue this model.

The molecule is illustrated in Fig. 3 and by formula (IV). As can be seen, it has *HH* stereochemistry. The fusion at the cyclobutane ring is of rare *cis, trans* type, the three bonds to S, C(4) and S′ lying on one side of the cyclobutane mean plane and that to C(4′) lying on the other (Table 7*a*). As can be seen from Table 7(*b*) the heterocyclic rings of dimer (5) have one boat and one chair conformation.



(IV)

The fact that the five independent dimer molecules in these crystals show such differing heterocyclic ring conformations could only be due to their inherent flexibility. The conformations adopted appear to be simply those which minimize intermolecular repulsions. There were no especially short distances found in any of the crystals.

As has been seen, because of disorder, it is not possible to classify dimer (4) as either *HH* or *HT*. The existence of a high-frequency IR carbonyl band at 1700 cm^{-1} would suggest the *HH* conformation.

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Structure of 1-{2-[2-(4-Hydroxyphenyl)ethylthio]ethyl}thymine

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Abstract. $C_{15}H_{18}N_2O_3S$, $M_r = 306{\cdot}38$, monoclinic, $P2_1/n$, $a = 9{\cdot}993\,(1)$, $b = 8{\cdot}475\,(1)$, $c = 17{\cdot}537\,(1)$ Å, $\beta = 91{\cdot}277\,(6)^\circ$, $V = 1484{\cdot}8\,(2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}361$, $D_x = 1{\cdot}370$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 19{\cdot}8$ cm^{-1}, $F(000) = 648$, $T = 293$ K, $R = 0{\cdot}057$ for 1989 observed reflexions. The molecule takes an extended form. Molecular dimensions of the thymine and phenol moieties are normal. The hydroxyl group of phenol hydrogen bonds with O(4) of the thymine moiety of the molecule at $\frac{1}{2}-x$, $-\frac{3}{2}+y$, $\frac{1}{2}-z$ [OH···O 2·778 (3) Å]. The three infinite chains so formed are assembled to give a triple helix, and the helices are connected side by side at thymine moieties by N(3)H···O(2) hydrogen bonds [2·862 (3) Å] to build up a $(10\bar{1})$ layer structure.

Introduction. As part of a series of studies on elementary binding patterns in protein–nucleic acid interactions, we have determined the structure of the model crystal that contains thymine and tyrosine skeletons. Direct interactions between nucleic acid base and tyrosine have not yet been found in crystal structures so far reported (Ohki, Takenaka, Shimanouchi & Sasada, 1977; Ogawa, Tago, Ishida & Tomita, 1980), although stacking and hydrogen bonding between them were suggested to occur in solution (Lancelot, 1977*a*,*b*; Hélène, Montenay-Garestier & Dimicoli, 1971).

Experimental. 1-(2-Mercaptoethyl)thymine synthesized from isothiourea and 1-(2-hydroxyethyl)thymine was condensed with 4-(2-chloroethyl)phenol to give the title compound in the presence of potassium *tert*-butoxide. Plate crystals from aqueous solution. D_m by flotation in mixture of dichloromethane and carbon tetrachloride. Rigaku four-circle diffractometer; graphite-mono-

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