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Crystal and Molecular Structure of Addition Products of Dimethyl Acetylene Dicarboxylate and N, N′- Thiocarbanilyl Hydrazine

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The compound was synthesized from a reaction between N, N'- dithiocarbanilyl hydrazine and dimethyl acetylene dicarboxylate. X-ray diffraction analysis of one of the reaction products in two different solvents gave triclinic crystals, [Space group= $P\bar{1}$. a= 13.273(8)Å, b= 19.16(10)Å, c= 10.965(4)Å, α= 95.73(4)°, β= 90.86(4)°, γ= 75.91(4)°, Z=4] and monoclinic crystals, [Space group= C2/c, a= 34.784(1)Å, b= 13.119(1) Å, c= 21.096(2) Å, α= 90°, β= 91.72(1)°, γ= 90°, Z=16] respectively. The carbo-methoxy in the triclinic form is cis to C = O in one molecule and trans in the other molecule while it is trans in both the molecules of the monoclinic form. There is a stacking of the five membered ring with phenyl rings in addition to the partial stacking between the five membered rings. The carbonyl groups point towards the centre of the heterocyclic five membered rings mimicking the O4′... base interaction in Z – DNA. The structure is stabilized by extensive intermolecular C-H...N, O-H...O and C-H...O hydrogen bonds. The solvent molecules also stabilize the packing of the molecules through hydrogen bonds.

Keywords: crystal structure; polymorphs; stacking interactions

INTRODUCTION

Thiazolidinones have useful biological activities. Thus etozolin, a 2-carbomethoxymethylidene-4-thiazolidinone has been developed much earlier as a diuretic[1] while more recently, troglitazone, a benzylthiazolidinedione has been

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introduced as an antidiabetic[2]. A facile and versatile route to construct thiazolidinones is a reaction of thioureas with acetylenedicarboxylic esters and we have shown that this affords unique products with E-carboalkoxy methylidene thiazolidinone structures[3]. We have extended the study to the reaction of N, N'-dithiocarbanilylhydrazine **1** with dimethyl acetylenedicarboxylate **2**. On the basis of our earlier experience, the reaction could lead to two symmetrical bisthiazolidinones **3** and **4** and an asymmetrical isomer **5** (Figure 1).

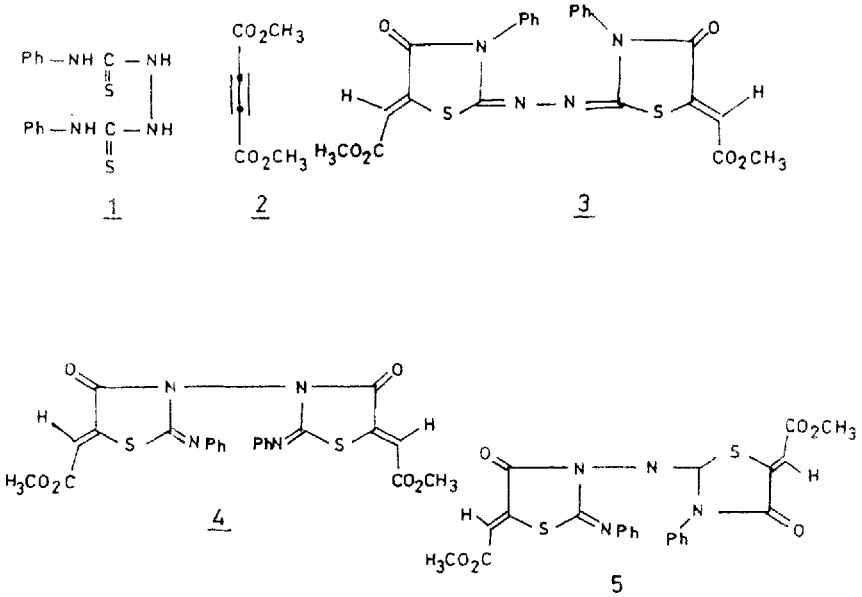

FIGURE 1 Chemical diagram of Reaction Compounds **1** – **5**

EXPERIMENTAL

Synthesis

From the reaction between **1** and **2**, we isolated in about 45% yield a mixture of **3** and **4**, a yellow powder, insoluble in most organic solvents except in boiling DMF, having a melting point above 280°C with mass at 522, corresponding to the molecular formula of $C_{24}H_{18}N_4O_6S_2$. Also from the product mixture we isolated acetone soluble crystalline compound **5** with a yield of 16%, melting point 221–4°C. This had a mass of 522 units, consistent with the molecular formula

$C_{24}H_{18}N_4O_6S_2$ and two ester methyl singlets in the proton NMR spectrum at 3.80 and 3.89. Crystals suitable for X-ray could not be obtained from the mixture of **3** and **4** but **5** was amenable. The crystal structure of **5** is reported here. Yellow coloured crystals of compound **5** were grown from two different solvents by slow evaporation at room temperature. Triclinic crystals (**I**) were obtained from aqueous propanol while monoclinic crystals (**II**) were from boiling DMF. The results obtained for the crystal structure of **I**and **II** are reported here.

Crystal structure of I

A yellow coloured rectangular crystal of dimension 0.2 × 0.1 × 0.1 mm was selected for X-ray data collection.All X-ray measurments were made at room temperature on an ENRAF-NONIUS (CAD-4 diffractometer)[4] using CuK_α radiation (λ=1.5418Å). The cell refinement and data reduction was done using CAD4-software[5]. The data were collected at 293 K using ($\omega/2\theta$) scanning mode. Least-squres refinement of 25 well-centered reflection in the range $8° \leq \theta \geq 22°$ yielded a primitive triclinic cell. During data collection three standard reflections periodically monitored showed no significant intensity variation. Corrections for Lorentz and polarisation factors were applied to intensity value but no absorption correction was made. A total of 11739 intensities were collected in the range $2.39° \leq \theta \geq 65.12°$ of which 8059 were unique (R_{int}=0.1172)

The structure was solved by direct methods SHELXS86 [6] and refined by full matrix least-squares method on $|F|^2$ using SHELXL93 [7]. Final refinement was carried out with anisotropic thermal parameters for all non H atoms. All the hydrogens were geometrically fixed and allowed to ride on corresponding carbon atoms. The final cycle of full matrix refinement based on 8025 observed reflections ($I>2\sigma I$) and 689 parameters converged to R =0.1054 with goodness of fit= 1.115. The largest peak and the deepest hole in the final difference map were 0.820 and –0.778e.$Å^{-3}$ respectively.

Crystal structure of II

A yellow coloured rectangular crystal of dimension 0.2 × 0.1 × 0.1 mm was selected for X-ray data collection. All X-ray measurments were made at room temperature on an ENRAF-NONIUS (CAD-4 diffractometer)[4] using MoK_α radiation (λ=0.71073Å). The cell refinement and data reduction was done using CAD4-software[5]. The data were collected at 293 K using ($\omega/2\theta$) scanning mode. Least-squres refinement of 25 well-centered reflection in the ranges $8° \leq \theta \geq 25°$ yielded monoclinic cell of space group C2/c. During data collection three standard reflections periodically monitored showed no significant intensity variation. Corrections for Lorentz and polarisation factors were applied to intensity

value but no absorption correction was made. A total of 9229 intensities were collected in the range $1.17° \leq \theta \geq 20.67°$ of which 4929 were unique(R_{int}=0.0352)

The structure was solved by direct methods SHELXS86 [6] and refined by full matrix least-squares method on $|F|^2$ using SHELXL93 [7]. Final refinement was carried out with anisotropic thermal parameters for all non H atoms. All the hydrogens were geometrically fixed and allowed to ride on corresponding carbon atoms. The final cycle of full matrix refinement based on 4929 observed reflections($I>2\sigma I$) and 654 parameters converged to R =0.0413 with goodness of fit= 0.916. The largest peak and the deepest hole in the final difference map were 0.178 and $-0.187 e.Å^{-3}$ respectively.

The fractional and atomic coordinates with equivalent isotropic displacement parameters for non-hydrogen atoms and bond lengths and bond angles for (**I**) and (**II**) are listed in Tables. Ia, Ib, IIa and IIb respectively. A perspective views of (**I**) and (**II**) with atom numbering are shown in Figures 2 and 3 respectively.

TABLE IA Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for structure **I**

Atom	*x*	*y*	*z*	*U(eq)*	*Occup*
S(1)	3572(2)	5429(1)	1663(2)	89(1)	
S(2)	-481(2)	3348(1)	1465(2)	80(1)	
O(1)	650(5)	5810(4)	975(7)	111(2)	
O(2)	1576(5)	2813(3)	-1800(5)	97(2)	
O(3)	-260(5)	1238(4)	343(6)	108(2)	
O(4)	-454(6)	2225(4)	1688(6)	116(2)	
O(5)	3874(5)	6804(3)	1304(6)	102(2)	
O(6)	2589(5)	7743(3)	840(7)	110(2)	
N(1)	2425(5)	4078(4)	2095(7)	92(2)	
N(2)	1968(5)	4869(4)	1436(6)	80(2)	
N(3)	1317(5)	4426(4)	1749(6)	86(2)	
N(4)	1608(4)	3688(3)	-209(5)	73(2)	
C(1)	2406(6)	5944(5)	1220(7)	81(2)	
C(2)	561(6)	5556(5)	1180(8)	83(2)	
C(3)	3002(6)	4693(5)	1782(7)	82(2)	
C(4)	4472(8)	3907(5)	2530(9)	96(3)	
C(5)	5248(8)	3424(7)	1800(12)	122(3)	
C(6)	6202(10)	3221(7)	2252(14)	133(4)	
C(7)	6456(11)	3462(8)	3390(16)	138(5)	

Atom	*x*	*y*	*z*	*U(eq)*	*Occup*
C(8)	5703(11)	3939(8)	4126(12)	131(4)	
C(9)	4695(9)	4170(6)	3683(11)	118(3)	
C(10)	1226(5)	3913(4)	948(7)	71(2)	
C(11)	733(6)	2789(4)	120(7)	78(2)	
C(12)	1344(6)	3071(4)	−787(8)	80(2)	
C(13)	2129(6)	4098(4)	−930(7)	77(2)	
C(14)	1532(6)	4668(5)	−1492(8)	88(2)	
C(15)	2057(8)	5064(6)	−2144(10)	115(3)	
C(16)	3131(8)	4879(6)	−2200(10)	110(3)	
C(17)	3696(7)	4309(5)	−1656(9)	100(3)	
C(18)	3200(6)	3896(4)	−1009(7)	82(2)	
C(19)	450(6)	2166(5)	−149(8)	85(2)	
C(20)	−115(7)	1892(5)	743(9)	92(2)	
C(21)	−855(11)	938(7)	1173(11)	146(5)	
C(22)	2204(7)	6637(5)	953(9)	98(3)	
C(23)	2976(7)	7069(5)	1056(9)	91(2)	
C(24)	3298(9)	8217(6)	1011(13)	136(5)	
S(1′)	2633(2)	−527(1)	−3773(2)	83(1)	
S(2′)	2649(2)	1104(1)	1597(2)	78(1)	
O(1′)	4485(5)	−965(3)	−1070(5)	93(2)	
O(2′)	3948(5)	2289(3)	−136(5)	91(2)	
O(3′)	2318(5)	1915(4)	3835(5)	101(2)	
O(4′)	2494(5)	3056(4)	4196(5)	107(2)	
O(5′)	3536(5)	−1774(4)	−5421(6)	104(2)	
O(6′)	5096(5)	−2499(4)	−5058(6)	108(2)	
N(1′)	1534(5)	620(4)	−2241(6)	82(2)	
N(2′)	3024(5)	−120(4)	−1516(5)	75(2)	
N(3′)	2808(5)	154(4)	−273(5)	83(2)	
N(4′)	3473(4)	1216(3)	−519(5)	70(1)	
C(1′)	3690(6)	−1031(4)	−3069(6)	72(2)	
C(2′)	3816(6)	−724(4)	−1777(6)	76(2)	
C(3′)	2302(6)	76(5)	−2435(6)	76(2)	
C(4′)	826(6)	841(5)	−3195(8)	88(2)	
C(5′)	−230(7)	966(6)	−2911(9)	109(3)	
C(6′)	953(9)	1231(8)	−3784(12)	138(4)	

Atom	*x*	*y*	*z*	*U(eq)*	*Occup*
C(7')	−648(10)	1386(8)	−4912(12)	136(4)	
C(8')	394(9)	1276(7)	−5144(11)	128(4)	
C(9')	1124(7)	1010(6)	−4275(9)	102(3)	
C(10')	3021(6)	771(4)	77(6)	73(2)	
C(11')	3093(6)	1869(4)	1449(6)	71(2)	
C(12')	3547(6)	1844(4)	216(6)	73(2)	
C(13')	3963(5)	1045(4)	1705(6)	68(2)	
C(14')	3977(6)	1341(5)	−2709(6)	81(2)	
C(15')	3963(7)	1172(5)	−3834(7)	90(2)	
C(16')	4942(7)	724(5)	−3955(7)	87(2)	
C(17')	5435(7)	438(5)	−2942(7)	90(2)	
C(18')	4964(6)	599(5)	1808(7)	81(2)	
C(19')	2999(6)	2437(4)	2278(7)	78(2)	
C(20')	2575(7)	2435(5)	3504(7)	86(2)	
C(21')	2081(11)	3064(7)	5424(9)	146(5)	
C(22')	4355(6)	−1639(5)	−3507(7)	82(2)	
C(23')	4270(7)	−1976(5)	−4756(8)	88(2)	
C(24')	5112(10)	−2873(8)	−6280(10)	142(5)	
O(1W)	7924(19)	2979(14)	6076(22)	376(12)	
O(2W)[a]	774(9)	4548(7)	4488(11)	132(4)	0.77
O(2W')[a]	10082(23)	4197(18)	4348(27)	94(8)	0.22
O(4A)	7990(8)	4887(6)	5341(10)	168(3)	
C(1A)	8255(14)	4319(11)	5673(16)	178(6)	
C(2A)	9150(11)	3544(8)	5651(13)	149(4)	
C(3A)	9397(11)	3147(8)	4252(13)	151(4)	

where $Ueq = 1/3\Sigma_i\Sigma_j a_i a_j a_i.a_j$

a. Disordered.

TABLE IB Bond lengths and bond angles for structure I

Atoms	*Length*
S(1)-C(1)	1.714(8)
S(1)-C(3)	1.771(8)
S(2)-C(11)	1.720(8)
S(2)-C(10)	1.769(7)

O(1)-C(2)	1.215(9)
O(2)-C(12)	1.183(9)
O(3)-C(20)	1.343(11)
O(3)-C(21)	1.460(11)
O(4)-C(20)	1.194(11)
O(5)-C(23)	1.215(10)
O(6)-C(23)	1.311(10)
O(6)-C(24)	1.459(12)
N(1)-C(3)	1.256(10)
N(1)-C(4)	1.433(11)
N(2)-C(3)	1.388(10)
N(2)-N(3)	1.416(8)
N(3)-C(10)	1.279(10)
N(4)-C(10)	1.362(9)
N(4)-C(12)	1.403(10)
N(4)-C(13)	1.458(9)
C(1)-C(22)	1.349(12)
C(1)-C(2)	1.487(11)
C(4)-C(9)	1.370(14)
C(4)-C(5)	1.403(15)
C(5)-C(6)	1.33(2)
C(6)-C(7)	1.35(2)
C(7)-C(8)	1.39(2)
C(8)-C(9)	1.40(2)
C(11)-C(19)	1.342(11)
C(11)-C(12)	1.510(10)
C(13)-C(14)	1.378(11)
C(13)-C(18)	1.381(11)
C(14)-C(15)	1.397(11)
C(15)-C(16)	1.384(14)
C(16)-C(17)	1.351(13)
C(17)-C(18)	1.392(11)
C(19) C(20)	1.452(11)
C(22)-C(23)	1.463(12)
S(1')-C(1')	1.719(8)
S(1')-C(3')	1.764(8)
S(2')-C(11')	1.731(7)
S(2')-C(10')	1.758(7)

O(1')-C(2')	1.206(9)
O(2')-C(12')	1.206(8)
O(3')-C(20')	1.219(10)
O(4')-C(20')	1.328(11)
O(4')-C(21')	1.458(11)
O(5')-C(23')	1.218(10)
O(6')-C(23')	1.313(11)
O(6')-C(24')	1.453(12)
N(1')-C(3')	1.272(10)
N(1')-C(4')	1.422(10)
N(2')-C(2')	1.370(10)
N(2')-C(3')	1.394(9)
N(2')-N(3')	1.418(8)
N(3')-C(10')	1.301(10)
N(4')-C(10')	1.374(9)
N(4')-C(12')	1.402(9)
N(4')-C(13')	1.434(8)
C(1')-C(22')	1.329(11)
C(1')-C(2')	1.503(10)
C(4')-C(9')	1.348(12)
C(4')-C(5')	1.397(12)
C(5')-C(6')	1.389(14)
C(6')-C(7')	1.39(2)
C(7')-C(8')	1.37(2)
C(8')-C(9')	1.391(14)
C(11')-C(19')	1.329(11)
C(11')-C(12')	1.479(10)
C(13')-C(14')	1.369(10)
C(13')-C(18')	1.393(10)
C(14')-C(15')	1.373(11)
C(15')-C(16')	1.372(12)
C(16')-C(17')	1.373(11)
C(17')-C(18')	1.373(11)
C(19')-C(20')	1.465(11)
C(22')-C(23')	1.470(11)
O(4A)-C(1A)	1.15(2)
C(1A)-C(2A)	1.66(2)
C(2A)-C(3A)	1.64(2)

Atoms	*Angle*
C(1)-S(1)-C(3)	90.3(4)
C(11)-S(2)-C(10)	90.7(4)
C(20)-O(3)-C(21)	115.0(9)
C(23)-O(6)-C(24)	115.7(8)
C(3)-N(1)-C(4)	121.6(7)
C(2)-N(2)-C(3)	117.2(7)
C(2)-N(2)-N(3)	120.8(6)
C(3)-N(2)-N(3)	118.6(6)
C(10)-N(3)-N(2)	116.9(6)
C(10)-N(4)-C(12)	116.3(6)
C(10)-N(4)-C(13)	124.5(6)
C(12)-N(4)-C(13)	118.6(6)
C(22)-C(1)-C(2)	120.2(7)
C(22)-C(1)-S(1)	126.9(6)
C(2)-C(1)-S(1)	112.9(6)
O(1)-C(2)-N(2)	125.0(7)
O(1)-C(2)-C(1)	126.3(8)
N(2)-C(2)-C(1)	108.7(7)
N(1)-C(3)-N(2)	121.2(7)
N(1)-C(3)-S(1)	128.1(7)
N(2)-C(3)-S(1)	110.6(6)
C(9)-C(4)-C(5)	120.4(10)
C(9)-C(4)-N(1)	120.1(10)
C(5)-C(4)-N(1)	119.3(9)
C(6)-C(5)-C(4)	119.0(12)
C(5)-C(6)-C(7)	122.7(13)
C(6)-C(7)-C(8)	119.3(12)
C(7)-C(8)-C(9)	119.7(13)
C(4)-C(9)-C(8)	118.9(12)
N(3)-C(10)-N(4)	133.9(6)
N(3)-C(10)-S(2)	113.6(5)
N(4)-C(10)-S(2)	112.5(5)
C(19)-C(11)-C(12)	121.0(8)
C(19)-C(11)-S(2)	126.5(6)
C(12)-C(11)-S(2)	112.4(6)
O(2)-C(12)-N(4)	125.7(7)
O(2)-C(12)-C(11)	126.4(8)

N(4)-C(12)-C(11)	107.9(7)
C(14)-C(13)-C(18)	123.3(7)
C(14)-C(13)-N(4)	118.6(7)
C(18)-C(13)-N(4)	118.1(7)
C(13)-C(14)-C(15)	117.2(8)
C(14)-C(15)-C(16)	120.0(9)
C(17)-C(16)-C(15)	121.5(8)
C(16)-C(17)-C(18)	120.2(8)
C(13)-C(18)-C(17)	117.8(8)
C(11)-C(19)-C(20)	120.5(8)
O(4)-C(20)-O(3)	124.2(8)
O(4)-C(20)-C(19)	124.0(8)
O(3)-C(20)-C(19)	111.8(8)
C(1)-C(22)-C(23)	123.3(8)
O(5)-C(23)-O(6)	126.0(8)
O(5)-C(23)-C(22)	121.2(8)
O(6)-C(23)-C(22)	112.8(8)
C(1′)-S(1′)-C(3′)	91.4(4)
C(11′)-S(2′)-C(10′)	90.7(3)
C(20′)-O(4′)-C(21′)	114.0(8)
C(23′)-O(6′)-C(24′)	116.5(8)
C(3′)-N(1′)-C(4′)	120.6(7)
C(2′)-N(2′)-C(3′)	117.4(6)
C(2′)-N(2′)-N(3′)	118.7(6)
C(3′)-N(2′)-N(3′)	121.6(7)
C(10′)-N(3′)-N(2′)	116.7(6)
C(10′)-N(4′)-C(12′)	113.2(6)
C(10′)-N(4′)-C(13′)	125.8(6)
C(12′)-N(4′)-C(13′)	120.5(6)
C(22′)-C(1′)-C(2′)	118.9(7)
C(22′)-C(1′)-S(1′)	128.8(6)
C(2′)-C(1′)-S(1′)	112.3(6)
O(1′)-C(2′)-N(2′)	125.0(7)
O(1′)-C(2′)-C(1′)	126.6(8)
N(2′)-C(2′)-C(1′)	108.4(6)
N(1′)-C(3′)-N(2′)	120.5(7)
N(1′)-C(3′)-S(1′)	129.0(6)
N(2′)-C(3′)-S(1′)	110.5(6)

C(9′)-C(4′)-C(5′)	120.0(8)
C(9′)-C(4′)-N(1′)	123.0(8)
C(5′)-C(4′)-N(1′)	116.6(8)
C(4′)-C(5′)-C(6′)	118.7(9)
C(5′)-C(6′)-C(7′)	121.5(11)
C(8′)-C(7′)-C(6′)	118.2(11)
C(7′)-C(8′)-C(9′)	120.7(11)
C(4′)-C(9′)-C(8′)	120.9(10)
N(3′)-C(10′)-N(4′)	132.3(7)
N(3′)-C(10′)-S(2′)	114.0(5)
N(4′)-C(10′)-S(2′)	113.7(5)
C(19′)-C(11′)-C(12′)	122.5(7)
C(19′)-C(11′)-S(2′)	126.3(6)
C(12′)-C(11′)-S(2′)	111.1(5)
O(2′)-C(12′)-N(4′)	122.7(6)
O(2′)-C(12′)-C(11′)	126.0(7)
N(4′)-C(12′)-C(11′)	111.3(6)
C(14′)-C(13′)-C(18′)	120.4(7)
C(14′)-C(13′)-N(4′)	120.7(7)
C(18′)-C(13′)-N(4′)	118.8(6)
C(13′)-C(14′)-C(15′)	119.7(8)
C(16′)-C(15′)-C(14′)	120.5(8)
C(15′)-C(16′)-C(17′)	119.6(7)
C(18′)-C(17′)-C(16′)	120.9(8)
C(17′)-C(18′)-C(13′)	118.8(7)
C(11′)-C(19′)-C(20′)	121.0(8)
O(3′)-C(20′)-O(4′)	124.2(8)
O(3′)-C(20′)-C(19′)	122.7(8)
O(4′)-C(20′)-C(19′)	113.1(8)
C(1′)-C(22′)-C(23′)	121.8(7)
O(5′)-C(23′)-O(6′)	125.5(8)
O(5′)-C(23′)-C(22′)	123.4(8)
O(6′)-C(23′)-C(22′)	111.1(8)
O(4A)-C(1A)-C(2A)	148.4(18)
C(3A)-C(2A)-C(1A)	111.9(11)

TABLE IIA Atomic coordinates and equivalent isotropic displacement parameters for structure II

Atom	*x*	*y*	*z*	*U(eq)*
S(1')	2809(1)	1358(1)	2732(1)	57(1)
S(2')	3819(1)	1327(1)	4249(1)	50(1)
O(1')	2825(1)	2416(2)	4433(1)	72(1)
O(2')	4545(1)	3007(2)	5178(1)	68(1)
O(3')	4128(1)	−574(2)	4547(1)	71(1)
O(4')	4646(1)	−822(2)	5176(2)	82(1)
O(5')	1755(1)	100(3)	3649(2)	124(1)
O(6')	2059(1)	459(2)	2775(1)	76(1)
N(1')	3528(1)	2191(2)	2635(1)	59(1)
N(2')	3217(1)	2353(2)	3583(1)	52(1)
N(3')	3479(1)	3079(2)	3840(1)	56(1)
N(4')	4023(1)	3220(2)	4493(1)	47(1)
C(1')	2624(1)	1524(3)	3485(2)	52(1)
C(2')	2886(1)	2144(3)	3900(2)	56(1)
C(3')	3237(1)	2032(3)	2958(2)	51(1)
C(4')	3528(1)	1855(3)	1992(2)	54(1)
C(5')	3776(1)	1099(3)	1823(2)	75(1)
C(6')	3787(1)	807(4)	1195(2)	87(1)
C(7')	3562(1)	1252(3)	743(2)	75(1)
C(8')	3319(1)	2016(4)	908(2)	79(1)
C(9')	3302(1)	2320(3)	1535(2)	76(1)
C(10')	3748(1)	2643(3)	4167(2)	47(1)
C(11')	4220(1)	1545(3)	4737(2)	48(1)
C(12')	4288(1)	2654(3)	4846(2)	52(1)
C(13')	3994(1)	4312(3)	4539(2)	49(1)
C(14')	3917(1)	4749(3)	5115(2)	60(1)
C(15')	3863(1)	5782(3)	5144(2)	75(1)
C(16')	3878(1)	6363(3)	4609(3)	82(1)
C(17')	3962(1)	5935(3)	4037(3)	81(1)
C(18')	4020(1)	4898(3)	4003(2)	69(1)
C(19')	4452(1)	838(3)	4991(2)	56(1)
C(20')	4388(1)	−247(3)	4874(2)	58(1)
C(21')	4590(1)	−1916(3)	5116(3)	108(2)
C(22')	2299(1)	1154(3)	3715(2)	61(1)

Atom	*x*	*y*	*z*	*U(eq),*
C(23')	2006(1)	531(3)	3387(2)	68(1)
C(24')	1772(2)	−120(4)	2406(2)	101(2)
S(1)	3045(1)	1346(1)	7036(1)	54(1)
S(2)	4413(1)	1356(1)	6739(1)	54(1)
O(1)	3660(1)	2280(2)	5668(1)	73(1)
O(2)	5282(1)	3146(2)	6681(1)	80(1)
O(3)	4812(1)	−511(2)	6754(1)	77(1)
O(4)	5455(1)	−643(2)	6743(1)	72(1)
O(5)	2455(1)	421(2)	6326(1)	86(1)
O(6)	2429(1)	314(2)	5268(1)	63(1)
N(1)	3556(1)	2322(2)	7833(2)	61(1)
N(2)	3676(1)	2294(2)	6750(1)	53(1)
N(3)	3965(1)	3057(2)	6796(1)	58(1)
N(4)	4625(1)	3277(2)	6742(1)	51(1)
C(1)	3158(1)	1462(3)	6239(2)	49(1)
C(2)	3521(1)	2043(3)	6164(2)	55(1)
C(3)	5126(1)	−129(3)	6719(2)	62(1)
C(4)	3296(1)	2031(3)	8312(2)	57(1)
C(5)	3355(1)	1145(3)	8644(2)	77(1)
C(6)	3101(2)	871(4)	9102(2)	92(2)
C(7)	2801(2)	1478(4)	9242(2)	91(2)
C(8)	2744(1)	2372(4)	8919(2)	92(1)
C(9)	2995(1)	2648(3)	8456(2)	77(1)
C(10)	4303(1)	2662(3)	6761(2)	50(1)
C(11)	4898(1)	1632(3)	6690(2)	52(1)
C(12)	4968(1)	2752(3)	6695(2)	58(1)
C(13)	4604(1)	4370(3)	6725(2)	56(1)
C(14)	4416(1)	4889(3)	7186(2)	82(1)
C(15)	4389(2)	5938(4)	7148(3)	99(2)
C(16)	4551(2)	6453(4)	6670(3)	94(2)
C(17)	4748(2)	5930(4)	6219(2)	93(2)
C(18)	4771(1)	4885(3)	6237(2)	74(1)
C(19)	5188(1)	972(3)	6671(2)	59(1)
C(20)	3457(1)	2060(2)	7279(2)	49(1)
C(21)	5426(1)	−1722(3)	6842(2)	86(2)

Atom	*x*	*y*	*z*	*U(eq).*
C(22)	2956(1)	1112(3)	5746(2)	57(1)
C(23)	2592(1)	583(3)	5819(2)	59(1)
C(24)	2043(1)	−96(4)	5289(2)	79(1)

where Ueq $=1/3\Sigma_i\Sigma_j a_i a_j a_i^* . a_j^*$

TABLE IIB Bond lengths and bond angles for structure **II**

Atoms	*Length*	*Atoms*	*Length*
S(1')-C(1')	1.745(3)	S(1)-C(1)	1.745(3)
S(1')-C(3')	1.782(4)	S(1)-C(20)	1.772(4)
S(2')-C(11')	1.735(3)	S(2)-C(11)	1.734(4)
S(2')-C(10')	1.752(4)	S(2)-C(10)	1.757(4)
O(1')-C(2')	1.204(4)	O(1)-C(2)	1.207(4)
O(2')-C(12')	1.212(4)	O(2)-C(12)	1.208(4)
O(3')-C(20')	1.201(4)	O(3)-C(3)	1.206(4)
O(4')-C(20')	1.323(4)	O(4)-C(3)	1.329(5)
O(4')-C(21')	1.452(5)	O(4)-C(21)	1.435(5)
O(5')-C(23')	1.188(4)	O(5)-C(23)	1.204(4)
O(6')-C(23')	1.314(5)	O(6)-C(23)	1.327(4)
O(6')-C(24')	1.460(5)	O(6)-C(24)	1.448(4)
N(1')-C(3')	1.256(4)	N(1)-C(20)	1.257(4)
N(1')-C(4')	1.426(4)	N(1)-C(4)	1.430(5)
N(2')-C(2')	1.378(5)	N(2)-C(2)	1.374(4)
N(2')-C(3')	1.387(4)	N(2)-C(20)	1.405(4)
N(2')-N(3')	1.414(4)	N(2)-N(3)	1.419(4)
N(3')-C(10')	1.279(4)	N(3)-C(10)	1.288(4)
N(4')-C(12')	1.383(4)	N(4)-C(10)	1.383(4)
N(4')-C(10')	1.387(4)	N(4)-C(12)	1.385(5)
N(4')-C(13')	1.440(4)	N(4)-C(13)	1.436(5)
C(1')-C(22')	1.335(5)	C(1)-C(22)	1.320(5)
C(1')-C(2')	1.487(5)	C(1)-C(2)	1.488(5)
C(4')-C(5')	1.369(5)	C(3)-C(19)	1.463(5)
C(4')-C(9')	1.370(5)	C(4)-C(9)	1.365(5)
C(5')-C(6')	1.380(6)	C(4)-C(5)	1.368(5)
C(6')-C(7')	1.349(6)	C(5)-C(6)	1.376(6)
C(7')-C(8')	1.362(6)	C(6)-C(7)	1.351(7)

C(8′)-C(9′)	1.383(6)	C(7)-C(8)	1.368(6)
C(11′)-C(19′)	1.331(5)	C(8)-C(9)	1.377(6)
C(11′)-C(12′)	1.491(5)	C(11)-C(19)	1.329(5)
C(13′)-C(14′)	1.376(5)	C(11)-C(12)	1.490(5)
C(13′)-C(18′)	1.373(5)	C(13)-C(14)	1.367(5)
C(14′)-C(15′)	1.369(5)	C(13)-C(18)	1.376(5)
C(15′)-C(16′)	1.365(6)	C(14)-C(15)	1.381(6)
C(16)-C(17′)	1.370(6)	C(15)-C(16)	1.352(6)
C(17′)-C(18′)	1.377(6)	C(16)-C(17)	1.371(6)
C(19′)-C(20′)	1.460(5)	C(17)-C(18)	1.373(6)
C(22′)-C(23′)	1.466(5)	C(22)-C(23)	1.455(5)
C(7)-C(8)-C(9)	119.5(5)	C(13)-C(14)-C(15)	119.3(4)
C(4)-C(9)-C(8)	120.5(4)	C(16)-C(15)-C(14)	120.7(5)
N(3)-C(10)-N(4)	120.6(3)	C(15)-C(16)-C(17)	119.7(4)
N(3)-C(10)-S(2)	126.4(3)	C(16)-C(17)-C(18)	120.8(4)
N(4)-C(10)-S(2)	113.0(3)	C(17)-C(18)-C(13)	118.9(4)
C(19)-C(11)-C(12)	121.2(3)	C(11)-C(19)-C(3)	121.8(4)
C(19)-C(11)-S(2)	127.3(3)	N(1)-C(20)-N(2)	122.5(3)
C(12)-C(11)-S(2)	111.4(3)	N(1)-C(20)-S(1)	127.7(3)
O(2)-C(12)-N(4)	124.8(3)	N(2)-C(20)-S(1)	109.9(3))
O(2)-C(12)-C(11)	124.7(4)	C(1)-C(22)-C(23)	121.8(3)
N(4)-C(12)-C(11)	110.5(3)	O(5)-C(23)-O(6)	124.1(3)
C(14)-C(13)-C(18)	120.6(4)	O(5)-C(23)-C(22)	123.3(4)
C(14)-C(13)-N(4)	120.3(3)	O(6)-C(23)-C(22)	112.7(3)
Atoms	*Angle*	*Atoms*	*Angle*
C(1′)-S(1′)-C(3′)	91.2(2)	C(18′)-C(13′)-N(4′)	119.6(3)
C(11′)-S(2′)-C(10′)	90.3(2)	C(15′)-C(14′)-C(13′)	118.9(4)
C(20′)-O(4′)-C(21′)	115.7(4)	C(16′)-C(15′)-C(14′)	120.4(4)
C(23′)-O(6′)-C(24′)	116.4(3)	C(15′)-C(16′)-C(17′)	120.9(4)
C(3′)-N(1′)-C(4′)	119.2(3)	C(16′)-C(17′)-C(18′)	119.1(4)
C(2′)-N(2′)-C(3′)	117.8(3)	C(13′)-C(18′)-C(17′)	119.8(4)
C(2′)-N(2′)-N(3′)	119.0(3)	C(11′)-C(19′)-C(20′)	121.5(4)
C(3′)-N(2′)-N(3′)	121.4(3)	O(3′)-C(20′)-O(4′)	124.1(4)
C(10′)-N(3′)-N(2′)	110.9(3)	O(3′)-C(20′)-C(19′)	123.8(4)
C(12′)-N(4′)-C(10′)	114.4(3)	O(4′)-C(20′)-C(19′)	112.1(4)
C(12′)-N(4′)-C(13′)	123.0(3)	C(1′)-C(22′)-C(23′)	128.1(4)
C(10′)-N(4′)-C(13′)	121.8(3)	O(5′)-C(23′)-O(6′)	123.4(4)

C(22′)-C(1′)-C(2′)	119.7(3)	O(5′)-C(23′)-C(22′)	123.8(4)
C(22′)-C(1′)-S(1′)	128.7(3)	O(6′)-C(23′)-C(22′)	112.7(4)
C(2′)-C(1′)-S(1′)	111.6(3)	C(1)-S(1)-C(20)	91.7(2)
O(1′)-C(2′)-N(2′)	124.6(3)	C(11)-S(2)-C(10)	90.6(2)
O(1′)-C(2′)-C(1′)	126.2(4)	C(3)-O(4)-C(21)	116.3(3)
N(2′)-C(2′)-C(1′)	109.2(3)	C(23)-O(6)-C(24)	116.4(3)
N(1′)-C(3′)-N(2′)	121.8(3)	C(20)-N(1)-C(4)	115.0(3)
N(1′)-C(3′)-S(1′)	128.1(3)	C(2)-N(2)-C(20)	116.9(3)
N(2′)-C(3′)-S(1′)	110.0(3)	C(2)-N(2)-N(3)	119.2(3)
C(5′)-C(4′)-C(9′)	119.5(4)	C(20)-N(2)-N(3)	120.1(3)
C(5′)-C(4′)-N(1′)	119.3(3)	C(10)-N(3)-N(2)	110.9(3)
C(9′)-C(4′)-N(1′)	121.1(3)	C(10)-N(4)-C(12)	114.4(3)
C(4′)-C(5′)-C(6′)	119.1(4)	C(10)-N(4)-C(13)	122.8(3)
C(7′)-C(6′)-C(5′)	121.8(4)	C(12)-N(4)-C(13)	122.6(3)
C(6′)-C(7′)-C(8′)	119.2(4)	C(22)-C(1)-C(2)	121.9(3)
C(7′)-C(8′)-C(9′)	120.1(4)	C(22)-C(1)-S(1)	126.8(3)
C(4′)-C(9′)-C(8′)	120.3(4)	C(2)-C(1)-S(1)	111.3(3)
N(3′)-C(10′)-N(4′)	120.4(3)	O(1)-C(2)-N(2)	124.2(3)
N(3′)-C(10′)-S(2′)	126.3(3)	O(1)-C(2)-C(1)	125.9(3)
N(4′)-C(10′)-S(2′)	113.3(3)	N(2)-C(2)-C(1)	109.9(3)
C(19′)-C(11′)-C(12′)	121.9(3)	O(3)-C(3)-O(4)	124.5(4)
C(19′)-C(11′)-S(2′)	126.3(3)	O(3)-C(3)-C(19)	123.4(4)
C(12′)-C(11′)-S(2′)	111.8(3)	O(4)-C(3)-C(19)	112.1(4)
O(2′)-C(12′)-N(4′)	125.1(3)	C(9)-C(4)-C(5)	119.6(4)
O(2′)-C(12′)-C(11′)	124.9(3)	C(9)-C(4)-N(1)	120.3(4)
N(4′)-C(12′)-C(11′)	110.0(3)	C(5)-C(4)-N(1)	120.0(4)
C(14′)-C(13′)-C(18′)	120.8(3)	C(4)-C(5)-C(6)	119.5(4)
C(14′)-C(13′)-N(4′)	119.5(3)	C(7)-C(6)-C(5)	120.9(4)
C(6)-C(7)-C(8)	119.9(4)	C(18)-C(13)-N(4)	119.1(3)

TABLE III Important torsion angles observed in molecules **A, B, C** and **D**

Bonds	*Molecule A*	*Molecule D*
	Angle(°)	Angle(°)
C(21) – O(3) – C(20) – O(4)	−1.7(1)	−3.2(1)
C(21) – O(4) – C(3) – C(19)	−177.9(1)	175.5(1)
C(24) – O(6) – C(23) – O(5)	−5.0(1)	7.2(1)
C(24) – O(6) – C(23) – C(22)	176.0(1)	−172.14(1)

C(4) – N(1) – C(3) – N(2)	–176.0(1)	179.4(1)
C(4) – N(1) – C(3) – S(1)	6.1(1)	–2.2(1)
C(3) – N(1) – C(4) – C(9)	74.3(1)	–86.9(1)
C(3) – N(1) – C(4) – C(5)	–110.5(1)	94.63(1)
C(10) – N(4) – C(13) – C(14)	–78.1(1)	55.5(1)
C(10) – N(4) – C(13) – C(18)	101.5(1)	–123.5(1)
C(1) – C(22) – C(23) – O(5)	5.6(1)	–1.02(1)
C(1) – C(22) – C(23) – O(6)	–175.1(1)	178.3(1)

Bonds	*Molecule B*	*Molecule C*
	Angle(°)	Angle(°)
C(21′) – O(4′) – C(20′) – O(3′)	1.2(1)	–2.2(1)
C(21′) – O(4′) – C(20′) – C(19′)	–179.5(1)	176.6(1)
C(24′) – O(6′) – C(23′) – O(5′)	–1.7(1)	5.64(1)
C(24′) – O(6′) – C(23′) – C(22′)	–179.5(1)	–177.46(1)
C(4′) – N(1′) – C(3′) – N(2′)	177.0(1)	–179.0(1)
C(4′) – N(1′) – C(3′) – S(1′)	–3.6(1)	3.71(1)
C(3′) – N(1′) – C(4′) – C(9′)	–57.0(1)	70.1(1)
C(3′) – N(1′) – C(4′) – C(5′)	131.0(1)	–114.1(1)
C(10′) – N(4′) – C(13′) – C14′	104.8(1)	110.10(1)
C(10′) – N(4′) – C(13′) – C(18′)	–78.3(1)	–66.0(1)
C(1′) – C(22) – C(23′) – O(5′)	–8.2(1)	167.6(1)
C(1′) – C(22′) – C(23′) – O(6′)	170.0(1)	–9.32(1)

RESULTS AND DISCUSSION

In the crystal structure of (**I**), there are two molecules of water (O1W and O2W) and one molecule of propanol (C1A, C2A, C3A and 04A). One of the water molecules, O2W is disordered. The bond lengths and bond angles are normal and the e.s. d's for (**I**) and (**II**) are 0.01Å, 0.7° and 0.007Å, 0.4° respectively. The C1-C2 bond length is short indicating that is bond has a partial double bond character. Table IV. gives some of the important torsion angles observed in the two crystal forms. In the monoclinic form, the carbo-methoxy groups in molecule (**C**) are in different conformation (viz) cis-cis and cis-trans, while in molecules (**A, B** and **D**) it is in trans-trans conformation. Energy minimization using BIOSYM software[8] with cff91 forcefield, was done to calculate the energy difference between the two conformations in molecule C. The two observed conformations (cis-cis and cis-trans) have an energy difference of 6.38 kcal/mol. In both the molecules of structure (**II**) the phenyl rings P5 to P8 deviate significantly from

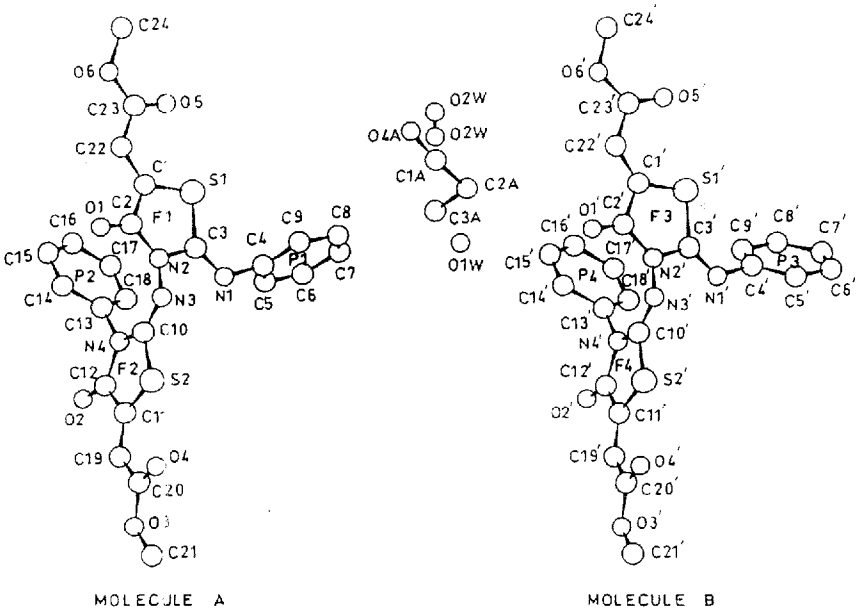

FIGURE 2 Perspective view of Structure **I** with atom numbering

planarity. However in structure (**I**) only one phenyl ring viz. P2 deviates signifi cantly from planarity. Also atoms of the five membered ring F3 lie in a plane

TABLE IV Intermolecular interaction of O1 and O1' of molecules **A**and **B** in structure **I**

Molecule A		
Contacts	*Distance (Å)*	*Symmetry*
O(1)...S(2)	3.40(1)	(1)
O(1)...N(4)	3.05(1)	(1)
O(1)...C(10)	3.22(1)	(1)
O(1)...C(11)	3.21(1)	(1)
O(1)...C(12)	3.00(1)	(1)
Molecule B		
Contacts	*Distance (Å)*	*Symmetry*
O(1')...N(4')	3.16(1)	(2)
O(1')...C(11')	3.28(1)	(2)
O(1')...C(12')	2.93(1)	(2)
O(1')...C(18')	3.3(1)	(2)

Equivalent positions (1) -x, -y+1, -z; (2) -x+1, -y, -z.

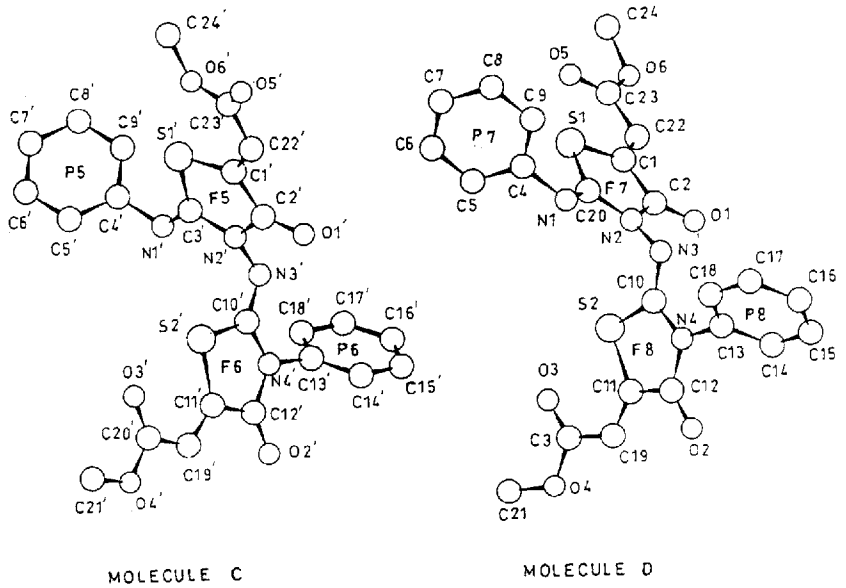

FIGURE 3 Perspective view of Structure II with atom numbering

INTER AND INTRA MOLECULAR INTERACTIONS

In molecule **B** of structure (**I**), the stacking occurs between the five membered ring F3 and the phenyl ring P4 with a stacking distance of 3.12 Å (Figure 4). Similarly, in structure (**II**), partial stacking of molecule **D** occurs between the five membered ring F8 with F8 of the symmetry related molecule (Figure 5), with a stacking distance of 3.48 Å. Stacking also occurs between the phenyl ring P8 with P8 of the symmetry related molecule, with a distance of 4.41 Å. Further, in (**I**), the carbonyl oxygen of the acetomethoxy group of both the molecules (**A** and **B**) point towards the centre of the heterocyclic rings F2 and F4 of the symmetry related molecule (Figure 4). This is reminiscent of O4′... base interactions in Z-DNA[9]. Table. IV gives the contacts made by O1 and O1′ of molecule **A** and **B** which has close interactions with the atoms of their respective five membered rings F2 and F4. However, in (**II**) only O1 of molecule **D** has close interactions with the five-membered ring F8 of molecule **C** (Figure 6). Table. V shows the interatomic interactions of O1 of molecule **D**. The packing of the molecules in (**I**) and (**II**) are stabilized by several C-H...O, C-H...N and O-H...O hydrogen bonds (Tables VI & VII).

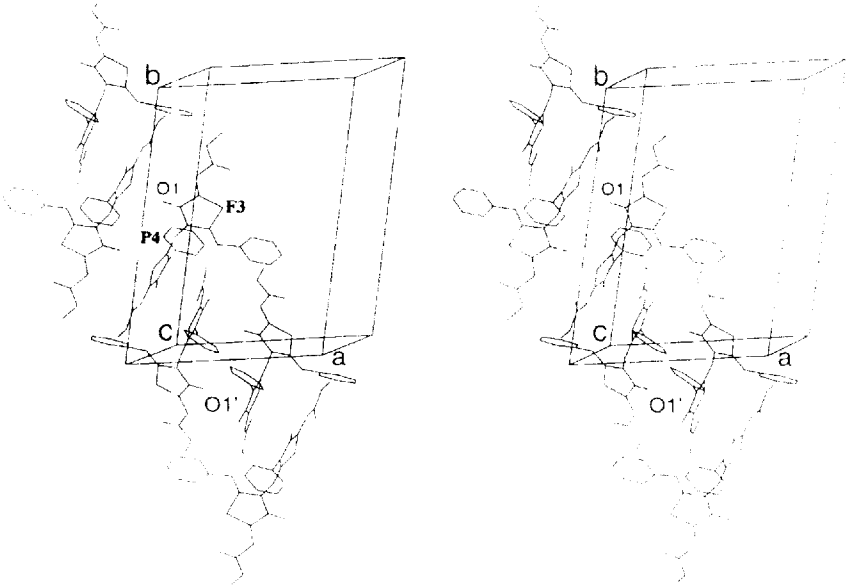

FIGURE 4 Stereoview of the stacking of the five-membered ring and the phenyl ring in molecule **B** of Structure **I**. Intermolecular interactions of O1 and O1' can also be seen

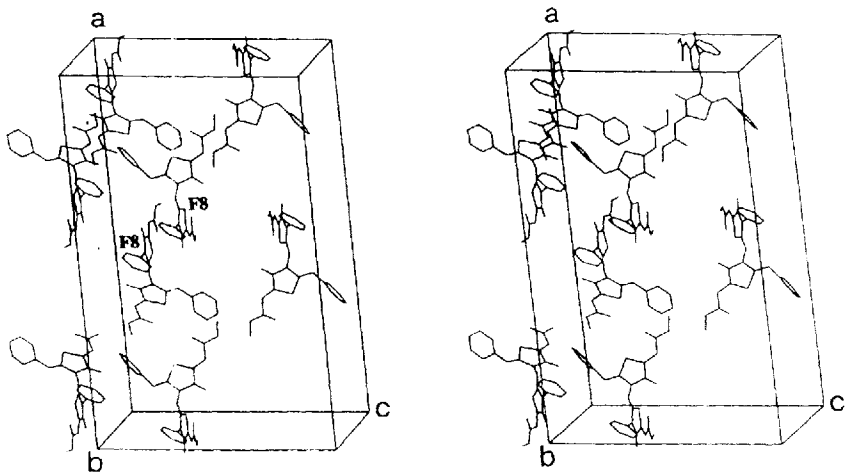

FIGURE 5 Stereoview of the partial stacking of five-membered ring in molecule **D** of structure **II** with its counter part in the symmetry related molecule

TABLE V Interatomic interaction of O1 of molecule **D**

Molecule D	
Contacts	*Distance (Å)*
O(1)...S(2′)	3.31(3)
O(1)...N(4′)	3.08(3)
O(1)...C(10′)	3.23(4)
O(1)...C(11′)	2.97(4)
O(1)...C(12′)	2.87(4)

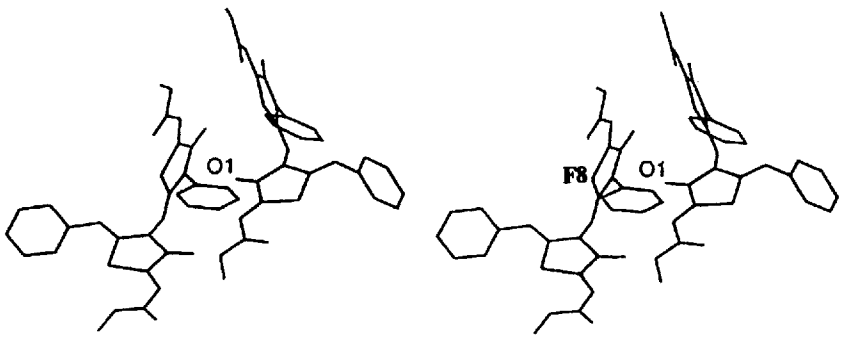

FIGURE 6 Stereoview of the interatomic interaction of O1 of molecule **D**with F8 of molecule **C**

TABLE VI Hydrogen bond geometry in Structure **I** and **II**

Structure I					
Donor (D)	*Acceptor (A)*	*D...A (Å)*	*H...A (Å)*	*D-H...A(°)*	*Symmetry*
C(18) – H(18)	H(18)...O(2′)	3.24(2)	2.37(2)	155.45(2)	(0)
C(14′) – H(14′)	H(14′)...O(2)	3.37(2)	2.52(2)	152.34(2)	(0)
C(19′) – H(19′)	H(19′)...N(1)	3.35(2)	2.45(2)	162.50(2)	(0)
C(19) – H(19)	H(19)...N(1′)	3.56(2)	2.74(2)	147.80(2)	(0)
Equivalent positions (0) x, y, z					
Structure II					
Donor (D)	*Acceptor (A)*	*D...A (Å)*	*H...A (Å)*	*D-H...A (°)*	*Symmetry*
C(7′) – H(7′)	H(7′)...O(3′)	3.37(2)	2.64(2)	135.20(2)	(1)
C(21′) – H(21B)	H(21B)...O(2′)	3.40(1)	2.58(1)	141.67(1)	(2)
C(22′) – H(22B)	H(22B)...O(6)	3.48(2)	2.77(2)	132.72(2)	(0)
C(22) – H(22D)	H(22D)...O(1′)	3.28(2)	2.59(2)	131.03(2)	(0)

Equivalent positions (0) x, y, z; (1)x, -y, z-1/2; (2) -x+1, -y, -z+1.

TABLE VII Intermolecular interaction of solvent atoms with the atoms of molecules Aand **B**

Interaction of the disordered water molecule O2W		
Contacts	*Distance (Å)*	*Symmetry*
O(2W)...O(4A)	2.85(1)	(1)
O(2W)...O(4A)	3.04(2)	(2)
O(2W)...C(1A)	2.95(2)	(3)
O(2W)...C(1A)	3.52(2)	(2)
O(2W)...C(2A)	2.93(2)	(3)
O(2W)...C(3A)	3.01(2)	(3)
Interaction of the water molecule O1W		
Contacts	*Distance (Å)*	*Symmetry*
O(1W)...C(22)	3.27(2)	(2)
O(1W)...C(23)	3.45(2)	(2)
O(1W)...O(5')	3.46(3)	(4)
O(1W)...C(6')	3.41(3)	(5)
O(1W)...C(7')	3.31(3)	(5)

Equivalent position: (1) x-1, y, z; (3) x-1, y, z-x+1, -y+1, -z+1; (4) -x+1, -y, -z; (5) x+1, y, z+1.

Acknowledgements

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