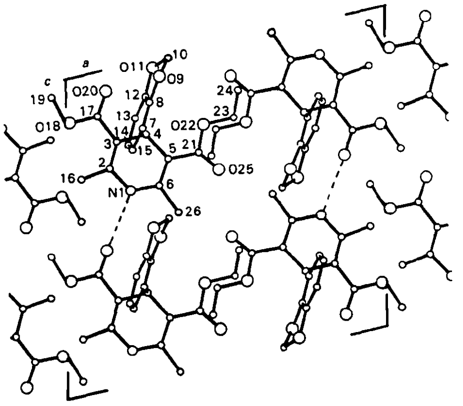

Fig. 2. Molecular packing viewed down **b**; hydrogen bonds are marked with dashed lines.

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Structure of 3,7-Dibromo-10-ethylphenothiazine

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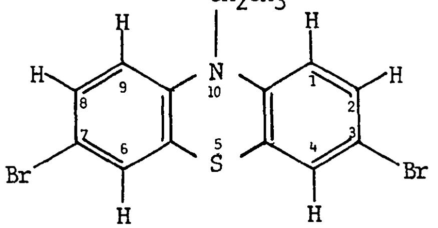
Abstract. $C_{14}H_{11}Br_2NS$, $M_r = 385{\cdot}1$, triclinic, $P\bar{1}$, $a = 8{\cdot}403\,(2)$, $b = 11{\cdot}405\,(2)$, $c = 15{\cdot}807\,(3)$ Å, $\alpha = 73{\cdot}93\,(1)$, $\beta = 102{\cdot}28\,(2)$, $\gamma = 83{\cdot}56\,(1)°$, $V = 1398{\cdot}6\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}829$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}70926$ Å, $\mu = 57{\cdot}86$ cm^{-1}, $F(000) = 752$, $T = 295$ K. Final $R = 0{\cdot}047$ for 3060 observed reflections. The folding angle between the benzo planes is 153·6 (2) and 145·3 (2)° for the two crystallographically independent molecules. The ethyl groups occupy quasi-equatorial positions relative to the central ring in both molecules; however, the configuration of the ethyl group is different in the two molecules.

Introduction. This paper reports the synthesis and structure of 3,7-dibromo-10-ethylphenothiazine (I) and is part of our continuing structural studies of substituted phenothiazines (Jovanovic, Biehl, de Meester & Chu, 1984). The objective of these studies is to determine the effect of the different substituents on the conformation and configuration of the phenothiazine ring system.



(I)

Experimental. The title compound was prepared by addition of 672 mg (2·1 mmol) of pyridium hydrobromide perbromide to a stirred solution of 227 mg

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(1 mmol) of 10-ethylphenothiazine in 25 ml of ethanol. The resulting solid was recrystallized from ethanol/water to yield colorless prisms (m.p. 347–348 K) of 3,7-dibromo-10-ethylphenothiazine. Accurate unit-cell parameters from least-squares refinement of 15 reflections in the range $20 < 2\theta < 30°$. Crystal dimensions 0·67 × 0·42 × 0·09 mm. Automatic Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\theta/2\theta$-scan mode, 4936 independent reflections collected to $2\theta = 50°$, *hkl* range: h −9→9, k −12→13, l 0→18, 3064 observed reflections with $I > 3\sigma(I)$, $\sigma(I)$ from counting statistics. Three standard reflections (400, 050 and 005) remeasured after every 100 reflections did not show any significant change during data collection. Lorentz and polarization corrections. Absorption correction, transmission factors on I ranged from 0·102 to 0·605. The structure was solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) which showed the positions of the Br, S and some C atoms. The remaining non-H atoms and later the H atoms were located on successive difference Fourier maps. Refinement by full-matrix least squares using *SHELX*76 (Sheldrick, 1976), anisotropic for non-H, isotropic for H atoms, $w = 1/[\sigma^2(F) + 3{\cdot}78\times10^{-4}F^2]$, $\sum w(|F_o| - |F_c|)^2$ minimized. Four strong reflections (200, 111, 113 and 114) with a large difference between F_o and F_c were excluded during the final refinement. $R = 0{\cdot}047$, $wR = 0{\cdot}046$. $(\Delta/\sigma)_{\max} = 0{\cdot}39$, $\Delta\rho_{\max} = 0{\cdot}50$, $\Delta\rho_{\min} = -0{\cdot}47$ e Å^{-3}, $S = 1{\cdot}43$, atomic scattering factors for C, H, N, S and Br and the anomalous-dispersion factors for S and Br from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters are give in Table 1.* The identification of the atoms and the configuration of the two crystallographically independent molecules are shown in the *ORTEP* (Johnson, 1965) drawing of Fig. 1. The central phenothiazine ring is in the boat conformation as shown by the torsion angles in Fig. 1 and the puckering parameters (Cremer & Pople, 1975). For molecule *A*, these parameters are $q_2 = 0{\cdot}439$ (6), $q_3 = 0{\cdot}088$ (6), $Q = 0{\cdot}448$ (6) Å, $\varphi_2 = 297{\cdot}6$ (8) and $\theta = 78{\cdot}66$ (7)°, while in molecule *B*, these parameters take the values 0·551 (6), 0·035 (6), 0·552 (6) Å, 300·6 (6) and 86·3 (6)°, respectively. For ideal boat conformation, the puckering parameters are $q_2 = Q$, $q_3 = 0$ Å, $\varphi_2 = 300$ and $\theta = 90°$. The ethyl substituents occupy quasi-equatorial positions with respect to the central ring; however, the configuration of the ethyl substituent is different for the two molecules as shown in Fig. 1 as well as the torsion angles about the N—C(11) bonds. The least-squares planes of the benzo rings and the deviations of the atoms from the least-squares planes are given in Table 3.* The tricyclic ring is folded along the S···N line with folding angles of 153·6 (2) and 145·1 (2)° for the two independent molecules. These values are larger than the value of 135·0° found in 10-ethylphenothiazine (Chu & van der

Table 1. *Fractional atomic coordinates and isotropic thermal parameters (e.s.d.'s in parentheses)*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{12}\cos\gamma + 2U_{13}\cos\beta + 2U_{23}\cos\alpha).$$

	x	y	z	U_{eq}/U_{iso}(Å^2)
C(1)*A*	0·2948 (10)	0·2459 (6)	0·1392 (4)	0·0644 (21)
C(2)*A*	0·3005 (10)	0·3611 (7)	0·0825 (4)	0·0685 (23)
C(3)*A*	0·3390 (9)	0·4521 (6)	0·1203 (5)	0·0606 (19)
Br(3)*A*	0·3387 (1)	0·6132 (1)	0·0420 (1)	0·0888 (3)
C(4)*A*	0·3806 (8)	0·4290 (6)	0·2130 (4)	0·0491 (16)
C(4a)*A*	0·3839 (8)	0·3115 (5)	0·2693 (4)	0·0434 (15)
S(5)*A*	0·4629 (2)	0·2812 (1)	0·3863 (1)	0·0510 (4)
C(5a)*A*	0·3542 (7)	0·1644 (5)	0·4271 (4)	0·0376 (14)
C(6)*A*	0·3248 (7)	0·1492 (5)	0·5126 (4)	0·0404 (16)
C(7)*A*	0·2562 (7)	0·0511 (5)	0·5510 (4)	0·0391 (14)
Br(7)*A*	0·2221 (1)	0·0287 (1)	0·6692 (1)	0·0586 (1)
C(8)*A*	0·2122 (8)	−0·0304 (5)	0·5038 (5)	0·0443 (16)
C(9)*A*	0·2354 (8)	−0·0152 (5)	0·4193 (4)	0·0459 (16)
C(9a)*A*	0·3066 (7)	0·0837 (5)	0·3774 (4)	0·0402 (16)
N(10)*A*	0·3339 (6)	0·0990 (4)	0·2913 (3)	0·0444 (13)
C(10a)*A*	0·3379 (7)	0·2172 (5)	0·2326 (4)	0·0439 (15)
C(11)*A*	0·3195 (9)	−0·0025 (5)	0·2512 (4)	0·0520 (17)
C(12)*A*	0·1434 (9)	−0·0080 (6)	0·2043 (5)	0·0679 (20)
C(1)*B*	0·0736 (8)	0·3288 (6)	0·8633 (4)	0·0496 (16)
C(2)*B*	0·0985 (8)	0·2054 (6)	0·9173 (4)	0·0475 (16)
C(3)*B*	0·2209 (8)	0·1212 (5)	0·9083 (4)	0·0423 (15)
Br(3)*B*	0·2629 (1)	−0·0479 (1)	0·9819 (1)	0·0647 (2)
C(4)*B*	0·3153 (8)	0·1568 (5)	0·8470 (4)	0·0408 (15)
C(4a)*B*	0·2899 (7)	0·2800 (5)	0·7957 (4)	0·0381 (14)
S(5)*B*	0·4192 (2)	0·3239 (1)	0·7218 (1)	0·0416 (3)
C(5a)*B*	0·2797 (7)	0·4527 (5)	0·6375 (4)	0·0352 (14)
C(6)*B*	0·2940 (8)	0·4816 (5)	0·5485 (4)	0·0451 (15)
C(7)*B*	0·1914 (8)	0·5850 (5)	0·4843 (4)	0·0432 (15)
Br(7)*B*	0·2153 (1)	0·6320 (1)	0·3635 (1)	0·0640 (2)
C(8)*B*	0·0729 (8)	0·6557 (6)	0·5065 (4)	0·0470 (16)
C(9)*B*	0·0590 (8)	0·6246 (6)	0·5954 (5)	0·0502 (17)
C(9a)*B*	0·1642 (8)	0·5249 (5)	0·6621 (4)	0·0428 (15)
N(10)*B*	0·1592 (7)	0·4945 (4)	0·7550 (4)	0·0479 (13)
C(10a)*B*	0·1725 (7)	0·3689 (5)	0·8042 (4)	0·0405 (14)
C(11)*B*	0·0783 (9)	0·5894 (6)	0·7863 (5)	0·0600 (19)
C(12)*B*	0·1642 (11)	0·7003 (7)	0·7764 (6)	0·0834 (25)
H(1)*A*	0·275 (6)	0·182 (3)	0·114 (3)	0·04 (1)
H(2)*A*	0·267 (7)	0·374 (5)	0·020 (1)	0·07 (2)
H(4)*A*	0·407 (6)	0·488 (4)	0·247 (3)	0·04 (1)
H(6)*A*	0·356 (7)	0·210 (5)	0·546 (4)	0·06 (2)
H(8)*A*	0·165 (6)	−0·090 (4)	0·525 (3)	0·04 (2)
H(9)*A*	0·187 (8)	−0·054 (6)	0·378 (5)	0·09 (2)
H(111)*A*	0·393 (7)	0·006 (5)	0·204 (4)	0·06 (2)
H(112)*A*	0·370 (6)	−0·085 (4)	0·310 (3)	0·04 (1)
H(121)*A*	0·136 (8)	−0·077 (5)	0·191 (4)	0·07 (2)
H(122)*A*	0·093 (10)	0·086 (7)	0·142 (5)	0·12 (3)
H(123)*A*	0·065 (8)	−0·021 (6)	0·239 (5)	0·08 (2)
H(1)*B*	−0·006 (6)	0·383 (4)	0·873 (3)	0·04 (1)
H(2)*B*	0·026 (8)	0·184 (5)	0·962 (4)	0·08 (2)
H(4)*B*	0·395 (6)	0·103 (4)	0·841 (3)	0·04 (1)
H(6)*B*	0·374 (7)	0·434 (5)	0·529 (4)	0·02 (1)
H(8)*B*	0·007 (6)	0·714 (4)	0·458 (3)	0·03 (1)
H(9)*B*	−0·021 (7)	0·670 (5)	0·609 (4)	0·01 (1)
H(111)*B*	−0·042 (9)	0·604 (6)	0·765 (5)	0·09 (2)
H(112)*B*	0·100 (7)	0·550 (5)	0·858 (4)	0·06 (2)
H(121)*B*	0·110 (8)	0·750 (5)	0·797 (4)	0·07 (2)
H(122)*B*	0·181 (10)	0·723 (7)	0·720 (6)	0·11 (3)
H(123)*B*	0·290 (11)	0·656 (8)	0·811 (6)	0·14 (3)

Standard deviations of U_{eq} calculated according to Schomaker & Marsh (1983).

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* Lists of structure factors, anisotropic thermal parameters and least-squares planes (Table 3) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43198 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

Helm, 1975); however, they are within the range of magnitudes found in other substituted phenothiazines (Chu & van der Helm, 1974, 1976, 1977; Jovanovic *et al.*, 1984). The difference in the magnitude of the folding angles and the different configuration of the ethyl substituents between the two crystallographically independent molecules of the title compound are due apparently to the effect of intermolecular interaction in the solid state. These effects have also been observed in other structures with two crystallographically independent molecules (Chu & van der Helm, 1976; Chu & Chung, 1976).

The bond lengths and bond angles are listed in Table 2. They are essentially identical in both molecules, except in the central ring. The C(9a)—N(10)—C(10a) angle of 121·8 (5)° in molecule *A* is greater than that of 118·4 (5)° found in molecule *B*. The average S—C bond lengths are 1·750 (6) and 1·775 (6) Å for molecules *A* and *B*, respectively.

The packing of the molecules in the unit cell is shown in the stereoscopic drawings of Fig. 2. There are no intermolecular distances less than the van der Waals distances. The shortest intermolecular contact between non-H atoms is S(5)*A*···C(8)*A* of 3·483 (7) Å.

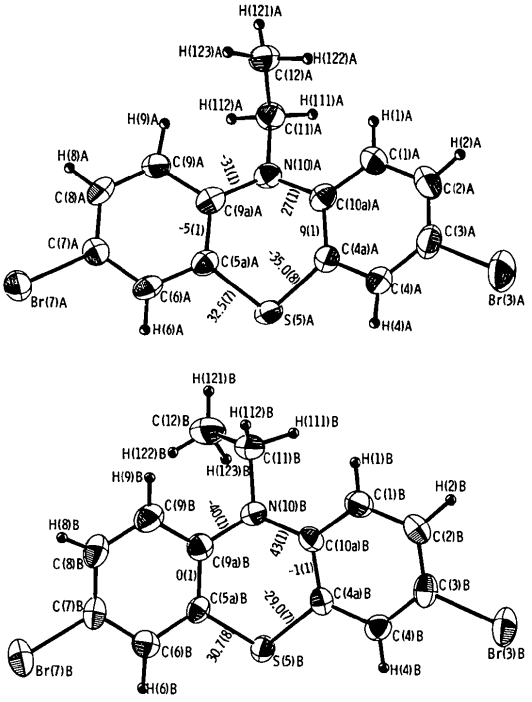

Fig. 1. *ORTEP* drawing of the two independent molecules *A* (top) and *B* with the torsion angles (°) around the central ring. Thermal ellipsoids are scaled at the 50% probability level. H atoms are represented as spheres of arbitrary radii. The torsion angles about the N(10)—C(11) bond are:

	Molecule *A*	Molecule *B*
C(9a)—N(10)—C(11)—C(12)	86·3 (8)°	−64 (1)°
C(10a)—N(10)—C(11)—C(12)	−79·2 (8)	139·4 (9)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

C(1)*A*—C(2)*A*	1·383 (11)	C(1)*B*—C(2)*B*	1·395 (9)
C(1)*A*—C(10a)*A*	1·377 (9)	C(1)*B*—C(10a)*B*	1·397 (9)
C(2)*A*—C(3)*A*	1·369 (11)	C(2)*B*—C(3)*B*	1·384 (9)
C(3)*A*—Br(3)*A*	1·910 (8)	C(3)*B*—Br(3)*B*	1·905 (6)
C(3)*A*—C(4)*A*	1·373 (10)	C(3)*B*—C(4)*B*	1·384 (9)
C(4)*A*—C(4a)*A*	1·382 (9)	C(4)*B*—C(4a)*B*	1·380 (9)
C(4a)*A*—S(5)*A*	1·747 (6)	C(4a)*B*—S(5)*B*	1·770 (6)
C(4a)*A*—C(10a)*A*	1·409 (9)	C(4a)*B*—C(10a)*B*	1·388 (8)
S(5)*A*—C(5a)*A*	1·753 (6)	S(5)*B*—C(5a)*B*	1·781 (6)
C(5a)*A*—C(6)*A*	1·393 (8)	C(5a)*B*—C(6)*B*	1·388 (9)
C(5a)*A*—C(9a)*A*	1·405 (8)	C(5a)*B*—C(9a)*B*	1·389 (9)
C(6)*A*—C(7)*A*	1·367 (8)	C(6)*B*—C(7)*B*	1·379 (9)
C(7)*A*—Br(7)*A*	1·902 (6)	C(7)*B*—Br(7)*B*	1·896 (6)
C(7)*A*—C(8)*A*	1·379 (9)	C(7)*B*—C(8)*B*	1·375 (9)
C(8)*A*—C(9)*A*	1·357 (9)	C(8)*B*—C(9)*B*	1·385 (10)
C(9)*A*—C(9a)*A*	1·405 (9)	C(9)*B*—C(9a)*B*	1·379 (10)
C(9a)*A*—N(10)*A*	1·395 (8)	C(9a)*B*—N(10)*B*	1·423 (8)
N(10)*A*—C(10a)*A*	1·418 (8)	N(10)*B*—C(10a)*B*	1·407 (8)
N(10)*A*—C(11)*A*	1·470 (8)	N(10)*B*—C(11)*B*	1·467 (9)
C(11)*A*—C(12)*A*	1·524 (10)	C(11)*B*—C(12)*B*	1·513 (12)
C(2)*A*—C(1)*A*—C(10a)*A*	122·1 (7)	C(2)*B*—C(1)*B*—C(10a)*B*	121·7 (6)
C(1)*A*—C(2)*A*—C(3)*A*	118·8 (7)	C(1)*B*—C(2)*B*—C(3)*B*	118·1 (6)
C(2)*A*—C(3)*A*—Br(3)*A*	119·0 (6)	C(2)*B*—C(3)*B*—Br(3)*B*	119·8 (5)
C(2)*A*—C(3)*A*—C(4)*A*	121·3 (7)	C(2)*B*—C(3)*B*—C(4)*B*	121·6 (6)
Br(3)*A*—C(3)*A*—C(4)*A*	119·7 (5)	Br(3)*B*—C(3)*B*—C(4)*B*	118·6 (5)
C(3)*A*—C(4)*A*—C(4a)*A*	119·3 (6)	C(3)*B*—C(4)*B*—C(4a)*B*	119·0 (6)
C(4)*A*—C(4a)*A*—S(5)*A*	117·6 (5)	C(4)*B*—C(4a)*B*—S(5)*B*	118·0 (5)
C(4)*A*—C(4a)*A*—C(10a)*A*	120·8 (6)	C(4)*B*—C(4a)*B*—C(10a)*B*	121·7 (6)
S(5)*A*—C(4a)*A*—C(10a)*A*	121·4 (5)	S(5)*B*—C(4a)*B*—C(10a)*B*	120·3 (5)
C(4a)*A*—S(5)*A*—C(5a)*A*	99·5 (3)	C(4a)*B*—S(5)*B*—C(5a)*B*	98·9 (3)
S(5)*A*—C(5a)*A*—C(6)*A*	118·1 (5)	S(5)*B*—C(5a)*B*—C(6)*B*	118·6 (5)
S(5)*A*—C(5a)*A*—C(9a)*A*	120·9 (5)	S(5)*B*—C(5a)*B*—C(9a)*B*	120·0 (5)
C(6)*A*—C(5a)*A*—C(9a)*A*	120·8 (5)	C(6)*B*—C(5a)*B*—C(9a)*B*	121·3 (6)
C(5a)*A*—C(6)*A*—C(7)*A*	119·9 (6)	C(5a)*B*—C(6)*B*—C(7)*B*	118·5 (6)
C(6)*A*—C(7)*A*—Br(7)*A*	119·5 (5)	C(6)*B*—C(7)*B*—Br(7)*B*	119·6 (5)
C(6)*A*—C(7)*A*—C(8)*A*	119·8 (6)	C(6)*B*—C(7)*B*—C(8)*B*	121·2 (6)
Br(7)*A*—C(7)*A*—C(8)*A*	120·6 (5)	Br(7)*B*—C(7)*B*—C(8)*B*	119·2 (5)
C(7)*A*—C(8)*A*—C(9)*A*	121·2 (6)	C(7)*B*—C(8)*B*—C(9)*B*	119·5 (6)
C(8)*A*—C(9)*A*—C(9a)*A*	121·0 (6)	C(8)*B*—C(9)*B*—C(9a)*B*	120·8 (6)
C(5a)*A*—C(9a)*A*—C(9)*A*	117·2 (5)	C(5a)*B*—C(9a)*B*—C(9)*B*	118·6 (6)
C(5a)*A*—C(9a)*A*—N(10)*A*	121·3 (5)	C(5a)*B*—C(9a)*B*—N(10)*B*	119·2 (6)
C(9)*A*—C(9a)*A*—N(10)*A*	121·5 (5)	C(9)*B*—C(9a)*B*—N(10)*B*	122·2 (6)
C(9a)*A*—N(10)*A*—C(10a)*A*	121·8 (5)	C(9a)*B*—N(10)*B*—C(10a)*B*	118·4 (5)
C(9a)*A*—N(10)*A*—C(11)*A*	119·3 (5)	C(9a)*B*—N(10)*B*—C(11)*B*	118·9 (5)
C(10a)*A*—N(10)*A*—C(11)*A*	117·3 (5)	C(10a)*B*—N(10)*B*—C(11)*B*	118·4 (5)
C(1)*A*—C(10a)*A*—C(4a)*A*	117·5 (6)	C(1)*B*—C(10a)*B*—C(4a)*B*	117·7 (6)
C(1)*A*—C(10a)*A*—N(10)*A*	122·5 (6)	C(1)*B*—C(10a)*B*—N(10)*B*	122·7 (6)
C(4a)*A*—C(10a)*A*—N(10)*A*	120·0 (5)	C(4a)*B*—C(10a)*B*—N(10)*B*	119·5 (5)
N(10)*A*—C(11)*A*—C(12)*A*	114·9 (5)	N(10)*B*—C(11)*B*—C(12)*B*	111·7 (6)

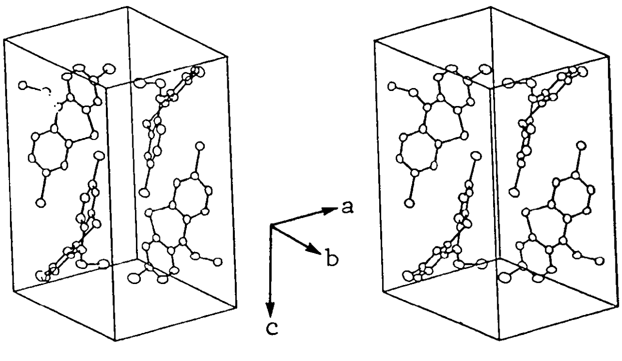

Fig. 2. Stereoscopic drawing of the molecular packing in the cell. The H atoms are omitted for clarity.

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Structure of (1S*,2R*)-2-(2-Furoyl)-2,5-dimethylcyclohex-5-en-1-yl Acetate

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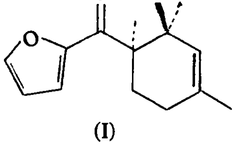
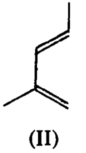
Abstract. $C_{15}H_{18}O_4$, $M_r = 262{\cdot}3$, monoclinic, $P2_1/n$, $a = 8{\cdot}797\,(1)$, $b = 20{\cdot}392\,(2)$, $c = 8{\cdot}916\,(1)$ Å, $\beta = 118{\cdot}33\,(1)°$, $V = 1407{\cdot}9\,(5)$ Å^3, $Z = 4$, $D_m = 1{\cdot}22\,(1)$, $D_x = 1{\cdot}237$ Mg m^{-3}, $\lambda(\text{Cu }K\alpha) = 1{\cdot}5418$ Å, $\mu(\text{Cu }K\alpha) = 0{\cdot}65$ mm^{-1}, $F(000) = 560$, room temperature, $R = 0{\cdot}046$ for 1942 observed reflections $[F > 3\sigma(F)]$. The title compound is a key intermediate in a projected trichodermin synthesis and was prepared by an *endo*-selective Diels–Alder reaction. Bond lengths and angles are normal. The formal C—C single bond of the furan ring is 1·412 (3) Å.

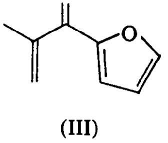
Introduction. As part of a programme dealing with the total synthesis of trichothecenes (Godtfredsen & Vangedal, 1964), the title compound (I) was prepared by a Diels–Alder reaction between 1-acetoxy-3-methyl-1,3-butadiene (II) and 1-(2-furanyl)-2-methyl-2-propen-1-one (III). Two likely products were anticipated for this reaction and since (I) is a key intermediate in the proposed route whose stereochemistry was vital, the X-ray structure determination was undertaken.



(I)



(II)



(III)

Experimental. Air-stable plate-like crystals were obtained from diethyl ether. Following photographic X-ray study, data collected from a crystal, 0·17 × 0·27 × 0·62 mm, D_m by flotation in CCl_4/heptane, Enraf–Nonius CAD-4 diffractometer, Ni-filtered Cu $K\alpha$ radiation. Data in the range $3 < \theta < 65°$ with h 0 to 10, k 0 to 23 and l −10 to 10. No decomposition with time was observed for three check reflections; empirical ψ-scan absorption correction (transmission: min. 92%, max. 99%), 1942 reflections with $F > 3\sigma(F)$ from a total of 2396 independent measurements. The structure was solved using *MULTAN*80 (Main *et al.*, 1980) and refinement carried out using *SHELX* (Sheldrick, 1976). The O atom of the acyl group was distinguished from the methyl group on the basis of bond lengths, and the O atom of the furan ring identified by bond-length criteria and isotropic thermal parameter refinement. After least-squares refinement using anisotropic thermal parameters the difference electron density synthesis showed the H-atom positions confirming the assignment of O and C. H atoms were introduced into the model with geometrically calculated positions $[d(\text{C—H}) = 1{\cdot}00$ Å$]$ and with two refined isotropic temperature factors (one for CH_3 groups and one for H atoms of CH and CH_2 groups). Least-squares refinement (on F) converged to $R = 0{\cdot}046$, $wR = 0{\cdot}070$, 183 parameters, $w = 1/[\sigma^2(F) + 0{\cdot}00055F^2]$, max. shift/e.s.d. = 0·5, residual electron density in the range −0·17 to 0·28 e Å^{-3}. Scattering factors and anomalous-dispersion corrections for O, C

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