0·022 (4) Å of their mean plane. Also angle *DEF* is always at the large end of the experimental range for angles in a cyclooctatetraene ring. However, the angle *EFG* has values between 134·4 (6) and 141·2 (4)° compared with the experimental average in cyclooctatetraene of 126·1° whereas angle *HAB* lies in the range 114·0 (5) to 122·6 (6)°. In each case the bond lengths decrease in the order $AH > HG > GF$ with differences of 3–4σ. Since the substitution pattern is quite different in (I) and (II), these observations appear to be features of octa-1,3,5-trienes in general. The dithiaocta-1,3,6-triene ring in the closely related 8,9-dimethyl-1,6-benzodithiocin (Barnes, Schroth & Moegel, 1978) has a twisted ring which does not resemble a cyclooctatetraene tub.

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Structures of the *s-cis* and *s-trans* Conformers of (*E*)-5-Methylthio-1,5-diphenyl-1-penten-3-one

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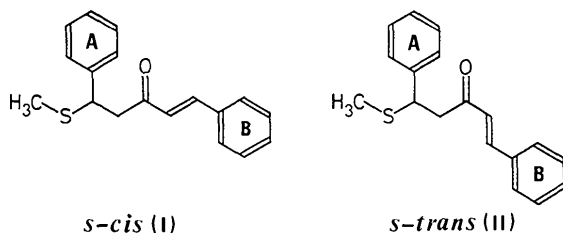
Abstract. (I) (*E*)-5-Methylthio-1,5-diphenyl-1-penten-s-cis-3-one, $C_{18}H_{18}OS$, $M_r = 282·4$, monoclinic, *Pc*, $a = 10·270$ (1), $b = 9·931$ (1), $c = 7·633$ (1) Å, $\beta = 98·31$ (1)°, $V = 770·3$ (1) Å^3, $Z = 2$, $D_x = 1·22$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 1·74$ mm^{-1}, $F(000) = 300$, $T = 293$ K, $R = 0·031$ for 1229 reflections. (II) (*E*)-5-Methylthio-1,5-diphenyl-1-penten-s-trans-3-one, $C_{18}H_{18}OS$, $M_r = 282·4$, monoclinic, *C*2/*c*, $a = 16·361$ (3), $b = 5·680$ (1), $c = 35·705$ (8) Å, $\beta = 112·81$ (1)°, $V = 3058·7$ (9) Å^3, $Z = 8$, $D_x = 1·23$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 1·76$ mm^{-1}, $F(000) = 1200$, $T = 293$ K, $R = 0·058$ for 1968 reflections. Molecules (I) and (II) have been found to have somewhat twisted s-cis and almost planar s-trans conformations, respectively (torsion angles −11·0 and 178·8°, respectively), for the α,β-unsaturated ketone system. The carbonyl and phenyl groups are in the *trans* configuration with respect to the C=C bond in the two conformers.

Introduction. A number of papers have been published on the conformations of α,β-unsaturated ketone derivatives. Some of the ketone derivatives are obtained either as the *s-cis* or as the *s-trans* form, mainly because of the steric and/or packing effect (Noack & Jones, 1961; Jungk & Schmidt, 1970; Ohkura, Kashino & Haisa, 1973; Rabinovich & Shakked, 1974), and others exist as equilibrium mixtures of different conformers at least in solution (Fuson, Josien & Shelton, 1954; Kronenberg & Havinga, 1965; Hayes & Timmons, 1968; Dimmock, Carter & Ralph, 1968; Silver & Boykin, 1970; Winecoff & Boykin, 1972).

Recently Tokuno (1985) has succeeded in obtaining two conformational isomers of (E)-5-methylthio-1,5-diphenyl-1-penten-3-one in crystalline states, and has suggested from the analyses of IR (KBr disk) spectra that one corresponds to the s-cis form and the other to the s-trans form. In order to confirm the conformations we carried out single-crystal X-ray analyses for both isomers.

s-cis (I)   s-trans (II)

Experimental. (I) Colorless plate crystals grown from ethanol at temperatures ranging from room temperature to 318 K; (II) colorless needle crystals grown from ethanol at temperatures higher than 328 K; D_m not determined; dimensions used for X-ray analyses: (I) $0.14 \times 0.14 \times 0.15$ mm, (II) $0.08 \times 0.09 \times 0.11$ mm; Rigaku automated four-circle diffractometer with rotating-anode X-ray generator, graphite monochromator, Cu $K\alpha$ radiation; lattice parameters from (I) 16 reflections with $20° < \theta < 39°$, (II) 20 reflections with $19° < \theta < 36°$; intensity data: $(\sin\theta)/\lambda <$ 0.575 Å^{-1}, (I) $-11 \le h \le 11$, $0 \le k \le 11$, $0 \le l \le 8$, (II) $0 \le h \le 18$, $0 \le k \le 6$, $-40 \le l \le 37$; ω–2θ scan, scan speed $4°$ min^{-1}, scan width $(\Delta\omega)$ (I) $1.5°$ + $0.15°\tan\theta$, (II) $0.9° + 0.15°\tan\theta$, at 40 kV and 200 mA; three standard reflections every 50 reflections, no significant variations; (I) 1514 independent reflections, 1229 observed $[|F| > 3\sigma(|F|)]$, (II) 2899 independent reflections, 1968 observed; Lorentz and polarization corrections, no absorption or extinction corrections; systematic absences: (I) $h0l$, $l = 2n+1$, (II) hkl, $h+k = 2n+1$, $h0l$, $l = 2n+1$; structures solved by direct methods using MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); full-matrix least squares using FMLS (Ashida, 1979), minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 0.0$ for $F_o = 0$ and $w = [\sigma^2(F)+a|F|+b|F|^2]^{-1}$ for $F_o \ne 0$ with (I) $a = 0.0$, $b = 0.0005$ and (II) $a = 0.07$, $b = 0.0001$; all H atoms located on difference Fourier maps and refined isotropically, non-H atoms refined anisotropically; (I) $R = 0.031$, $wR = 0.040$, $S = 2.29$, $(\Delta/\sigma)_{max} = 0.1$, (II) $R = 0.058$, $wR = 0.075$, $S = 1.39$, $(\Delta/\sigma)_{max} = 0.1$; electron density in final difference Fourier maps using SFFR (Ashida, 1979): (I) ± 0.2, (II) ± 0.3 e Å^{-3}; atomic scattering factors and anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974); data collections and numerical calculations performed at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Discussion. The final atomic coordinates and isotropic thermal parameters for (I) and (II) are listed in Tables 1 and 2, respectively, and views of the two conformers with the atom numbering are shown together in Fig. 1.*

Molecule (I) is found to have an s-cis conformation for the α,β-unsaturated ketone system, with a torsion angle of -11.0 (5)°. On the other hand, molecule (II) has an s-trans conformation for the ketone system, with a torsion angle of 178.8 (6)°. This almost planar s-trans conformation for (II) is consistent with the low frequency of the carbonyl stretching band observed in (II) (1646 cm^{-1}; Tokuno, 1985). The carbonyl and phenyl groups are in the trans configuration with respect to the C(11)—C(12) double bond in both molecules.

Bond distances are very similar in the two conformers, as shown in Table 3. For instance, the differences in the S—CH$_3$, the average aromatic C—C in phenyl rings A and B, the C=O, C—C and C=C distances in the α,β-unsaturated ketone moiety between the two molecules are 0.008, 0.004, 0.005, 0.000, 0.016 and 0.013 Å, respectively, and lie within 3σ. The C—H distances range from 0.82 to 1.08 Å (e.s.d. $\sim$0.05 Å) for (I) and from 0.86 to 1.16 Å (e.s.d. $\sim$0.05 Å) for (II), which are accepted values for the normal C—H bond.

Principal bond angles in (I) and (II) are given together in Table 4. There are significant differences between the trigonal C—C—C and C—C—O angles in the α,β-unsaturated ketone moiety of the two conformers. In molecule (I) the angles C(9)—C(10)—C(11), O—C(10)—C(11), C(10)—C(11)—C(12) and C(11)—C(12)—C(13) are 115.5 (2), 122.5 (3), 122.2 (3) and 127.6 (3)°, respectively, while in molecule (II) the corresponding angles are 120.7 (3), 116.6 (3), 127.7 (4) and 123.9 (4)°, respectively. The opening of the C(11)—C(12)—C(13) angle in both conformers is ascribed to the short intramolecular nonbonded H(C11)···H(C14) contact: 2.29 (7) Å in (I) and 2.08 (6) Å in (II). The H(C11)···H(C14) contacts in both conformers also produce considerable twists about the C(12)—C(13) bond, at the expense of the conjugation energy of the system; the angle between the C(10)—C(11)—C(12) plane and the phenyl ring B is 7.1 (5)° for (I) and 17.3 (6)° for (II). There exists another close intramolecular nonbonded H···H contact in molecule (II), H'(C9)···H(C12)|2.02 (7) Å|, and the relaxation of the H'(C9)···H(C12) repulsion is

achieved mainly by the opening of the C(10)—C(11)—C(12) angle to 127·7 (4)°.

The aromatic bond angles show no significant deviations from 120° except at the substituted atoms, C(3) and C(13), where smaller values are observed in both (I) and (II). This deviation from 120° is consistent with the observation that the aromatic substitution by an electron-donating group leads to an internal angle smaller than 120° on the substituted C (Carter, McPhail & Sim, 1966; Hope, 1969).

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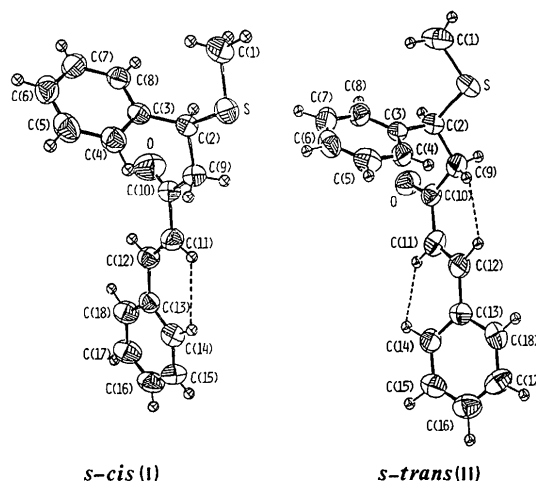

s–cis (I)   s–trans (II)

Fig. 1. *ORTEP*II (Johnson, 1976) drawings of the s-cis (I) and s-trans (II) forms with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level for the non-H atoms, and are arbitrarily represented as a sphere for the H atoms. Dashed lines indicate short interatomic H···H contacts.

Table 1. *Fractional coordinates* $(\times 10^4)$ *and isotropic temperature factors for the s-cis form* (I) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j B_{ij}(\mathbf{a}_i\cdot\mathbf{a}_j).$$

	x	y	z	$B_{eq}(\text{Å}^2)$
S	0	6319 (1)	0	4·49 (2)
O	1103 (2)	9153 (2)	−4281 (3)	6·7 (1)
C(1)	−998 (5)	7163 (5)	1389 (5)	6·2 (1)
C(2)	127 (3)	7597 (3)	−1692 (3)	3·4 (1)
C(3)	−1202 (3)	7918 (3)	−2726 (3)	3·3 (1)
C(4)	−1856 (3)	7014 (3)	−3932 (4)	4·3 (1)
C(5)	−3073 (3)	7332 (4)	−4867 (5)	5·1 (1)
C(6)	−3663 (3)	8558 (4)	−4605 (4)	5·2 (1)
C(7)	−3031 (3)	9438 (4)	−3407 (4)	4·9 (1)
C(8)	−1806 (3)	9140 (3)	−2473 (4)	4·0 (1)
C(9)	1124 (3)	7042 (3)	−2812 (4)	3·7 (1)
C(10)	1467 (3)	7993 (3)	−4205 (4)	3·7 (1)
C(11)	2311 (3)	7425 (3)	−5442 (4)	4·1 (1)
C(12)	2547 (3)	8077 (3)	−6868 (4)	3·9 (1)
C(13)	3383 (3)	7647 (3)	−8169 (4)	3·8 (1)
C(14)	3953 (3)	6368 (3)	−8142 (4)	4·9 (1)
C(15)	4784 (4)	6045 (5)	−9331 (6)	6·0 (1)
C(16)	5054 (3)	6962 (5)	−10599 (5)	5·8 (1)
C(17)	4452 (4)	8207 (4)	−10689 (5)	5·5 (1)
C(18)	3630 (3)	8549 (3)	−9473 (4)	4·8 (1)

Table 2. *Fractional coordinates* $(\times 10^4)$ *and isotropic temperature factors for the s-trans form* (II) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j B_{ij}(\mathbf{a}_i\cdot\mathbf{a}_j).$$

	x	y	z	$B_{eq}(\text{Å}^2)$
S	3983 (1)	2130 (2)	5708·7 (3)	6·31 (4)
O	3687 (2)	−3274 (4)	6589 (1)	5·6 (1)
C(1)	3559 (4)	740 (13)	5225 (2)	7·1 (2)
C(2)	3534 (2)	171 (7)	5987 (1)	4·4 (1)
C(3)	2538 (2)	499 (6)	5850 (1)	3·6 (1)
C(4)	2176 (3)	2516 (7)	5945 (1)	4·6 (1)
C(5)	1260 (3)	2742 (7)	5816 (1)	5·1 (1)
C(6)	708 (3)	1010 (8)	5592 (1)	5·1 (1)
C(7)	1067 (3)	−974 (8)	5494 (1)	5·2 (1)
C(8)	1974 (2)	−1210 (7)	5623 (1)	4·4 (1)
C(9)	4037 (3)	593 (7)	6439 (1)	4·6 (1)
C(10)	3807 (2)	−1222 (6)	6687 (1)	3·9 (1)
C(11)	3729 (2)	561 (6)	7078 (1)	4·5 (1)
C(12)	3842 (2)	1513 (7)	7248 (1)	4·4 (1)
C(13)	3755 (2)	1991 (6)	7633 (1)	3·9 (1)
C(14)	3320 (2)	505 (7)	7807 (1)	4·3 (1)
C(15)	3252 (3)	1081 (8)	8168 (1)	5·2 (1)
C(16)	3607 (3)	3089 (8)	8367 (1)	5·7 (1)
C(17)	4037 (3)	4579 (8)	8208 (1)	5·5 (1)
C(18)	4113 (2)	4105 (7)	7844 (1)	4·7 (1)

Table 3. *Bond distances* (Å) *in the s-cis* (I) *and s-trans* (II) *forms* (*except those for* C—H), *with e.s.d.'s in parentheses*

	s-cis	s-trans		s-cis	s-trans
S—C(1)	1·786 (5)	1·778 (7)	C(10)—O	1·211 (4)	1·211 (5)
S—C(2)	1·829 (3)	1·826 (4)	C(10)—C(11)	1·482 (4)	1·498 (5)
C(2)—C(3)	1·509 (4)	1·520 (5)	C(11)—C(12)	1·318 (4)	1·305 (6)
C(2)—C(9)	1·528 (4)	1·518 (6)	C(12)—C(13)	1·467 (4)	1·460 (5)
C(3)—C(4)	1·388 (4)	1·391 (5)	C(13)—C(14)	1·397 (4)	1·396 (5)
C(3)—C(8)	1·389 (4)	1·367 (5)	C(13)—C(18)	1·389 (4)	1·419 (6)
C(4)—C(5)	1·383 (4)	1·391 (6)	C(14)—C(15)	1·371 (6)	1·374 (6)
C(5)—C(6)	1·387 (6)	1·365 (6)	C(15)—C(16)	1·385 (7)	1·351 (7)
C(6)—C(7)	1·360 (6)	1·377 (6)	C(16)—C(17)	1·380 (6)	1·356 (7)
C(7)-C(8)	1·385 (4)	1·379 (6)	C(17)—C(18)	1·384 (5)	1·380 (6)
C(9)—C(10)	1·502 (4)	1·499 (6)			

Table 4. *Bond angles* (°) *in the s-cis* (I) *and s-trans* (II) *forms* (*except those involving* H), *with e.s.d.'s in parentheses*

	s-cis	s-trans
C(1)—S—C(2)	101·5 (2)	99·8 (3)
S—C(2)—C(3)	111·4 (2)	110·9 (3)
S—C(2)—C(9)	105·5 (2)	108·4 (3)
C(3)—C(2)—C(9)	114·4 (2)	113·3 (3)
C(2)—C(3)—C(4)	121·6 (2)	121·8 (3)
C(2)—C(3)—C(8)	120·0 (2)	119·8 (3)
C(4)—C(3)—C(8)	118·3 (3)	118·4 (3)
C(3)—C(4)—C(5)	120·6 (3)	120·0 (4)
C(4)—C(5)—C(6)	120·5 (4)	120·7 (4)
C(5)—C(6)—C(7)	119·0 (4)	119·2 (4)
C(6)—C(7)—C(8)	121·2 (4)	120·2 (4)
C(3)—C(8)—C(7)	120·4 (3)	121·4 (4)
C(2)—C(9)—C(10)	114·5 (2)	111·3 (3)
C(9)—C(10)—O	122·0 (3)	122·7 (4)
C(9)—C(10)—C(11)	115·5 (2)	120·7 (3)
O—C(10)—C(11)	122·5 (3)	116·6 (3)
C(10)—C(11)—C(12)	122·2 (3)	127·7 (4)
C(11)—C(12)—C(13)	127·6 (3)	123·9 (4)
C(12)—C(13)—C(14)	122·7 (3)	124·0 (3)
C(12)—C(13)—C(18)	118·8 (3)	119·2 (3)
C(14)—C(13)—C(18)	118·5 (3)	116·8 (3)
C(13)—C(14)—C(15)	120·2 (3)	120·9 (4)
C(14)—C(15)—C(16)	121·0 (4)	121·3 (4)
C(15)—C(16)—C(17)	119·4 (4)	119·6 (5)
C(16)—C(17)—C(18)	119·9 (4)	121·5 (4)
C(13)-C(18)—C(17)	121·0 (3)	119·8 (4)

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Structure of the 2R,3R/2S,3S Diastereoisomer of 1-(2-Fluorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl)-3-pentanol

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Abstract. $C_{15}H_{20}FN_3O$, $M_r = 277.3$, $P2_1/c$, $a = 9.500$ (4), $b = 12.389$ (5), $c = 13.019$ (5) Å, $\beta = 101.92$ (3)°, $V = 1499.2$ Å^3, $Z = 4$, $D_m = 1.25$ (2), $D_x = 1.23$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.53$ cm^{-1}, $F(000) = 592$, room temperature, final $R = 0.047$ for 1364 observed reflections. The carbon atoms of the pentanol function adopt an extended 'W' conformation and the atoms are essentially coplanar. The triazolyl ring, which shows significant delocalization, and the fluorophenyl ring are twisted well out of the plane of the pentanol carbon chain. The exocyclic angles of the triazolyl ring are very asymmetric with C—N—C, 129.9 (3)°, significantly larger than C—N—N, 120.6 (3)°. There is intermolecular hydrogen bonding between the 4-aza N atom of the triazolyl ring and the hydroxyl group of a neighbouring molecule, N···H(O) = 1.88 Å, such that molecules of the 2R,3R and 2S,3S configurations are linked alternately into chains.

Introduction. The title compound is an analogue of the systemic fungicide diclobutrazol (Balasubramanyan & Shephard, 1975). The mode of action is believed to be the inhibition of fungal ergosterol biosynthesis and the *RR,SS* diastereoisomer is more active than the *RS,SR* diastereoisomer (Gadher, Mercer, Baldwin & Wiggins, 1983). Structure–activity relationships indicate that the triazolyl and hydroxyl groups play important roles while the substituents in the phenyl ring may have significant effects on molecular conformation and lipophilicity (Marchington, 1978). Thus, we have determined the crystal structure of the title compound to establish its solid-state conformation as part of a programme to study the relationship between conformation and biological activity in this series of fungicides. A preliminary description of this structure has already been published (Anderson, Branch, Loeffler, Mann, Nowell & Walker, 1984).

Experimental. Recrystallization from ethanol:water (2:1); D_m by flotation in hexane/CCl$_4$; clear colourless

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