was by full-matrix least-squares methods. Most of the calculations were performed on a VAX 6420 computer at the Instituto de Física e Química de Sao Carlos.

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D-Secoestrone Derivatives. II. 16-Cyano-3-methoxy-16,17-secoestra-1,3,5(10)-trien-17-yl *p*-Toluenesulfonate

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Abstract

The asymmetric unit contains two molecules, which differ slightly in the geometry of their toluenesul-

fonyloxy moieties. The strong dipole–dipole repulsion between the sulfonyl and nitrile groups determines the conformation of these parts of the molecules.

Comment

The title compound was synthesized as a crucial intermediate in the preparation of some 17-deoxy-17-halogeno-D-secoestrone derivatives (Petrović, Pejanović, Miljković & Hranisavljević, 1990). However, this compound did not show any estrogenic or antiestrogenic activity. The structures of the chloro, bromo and iodo derivatives have already been published (Stanković, Petrović, Miljković, Pejanović, Kovačević, Stefanović & Bruvo, 1992).

A perspective view of the symmetry-independent molecule A, computed from the final atomic coordinates listed in Table 1, is shown in Fig. 1. Selected bond lengths, angles and torsion angles are given in Table 2. As the starting material was synthesized from natural estrone, the absolute stereochemistry of which is known (Fieser & Fieser, 1967), it was assumed, for the purposes of the X-ray structure refinement, that the same enantiomorph occurs in the crystalline state.
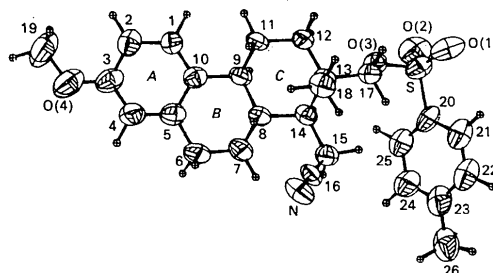

Fig. 1. A perspective view of the symmetry independent molecule A.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å²)

$$U_{eq} = \tfrac{1}{3}[(U_{11} + U_{33})\sin^{-2}\beta + U_{22} + 2U_{13}\sin^{-2}\beta\cos\beta].$$

	x	y	z	U_{eq}
S(1A)	0.3532 (1)	0.3984 (3)	0.8754 (2)	0.071 (0)
O(1A)	0.3164 (2)	0.5155 (8)	0.8611 (5)	0.094 (2)
O(2A)	0.3943 (2)	0.4650 (8)	0.8479 (5)	0.096 (2)
O(3A)	0.3611 (1)	0.3375 (6)	1.0213 (4)	0.064 (1)
O(4A)	0.5066 (2)	−0.2589 (10)	1.8457 (6)	0.110 (2)
N(1A)	0.2852 (2)	−0.3127 (8)	1.2106 (6)	0.081 (2)
C(1A)	0.4589 (2)	0.0733 (10)	1.6176 (6)	0.063 (2)
C(2A)	0.4816 (2)	0.0039 (11)	1.7299 (7)	0.071 (2)
C(3A)	0.4849 (2)	−0.1764 (12)	1.7401 (8)	0.074 (2)
C(4A)	0.4670 (2)	−0.2736 (11)	1.6370 (8)	0.078 (2)
C(5A)	0.4451 (2)	−0.2032 (9)	1.5239 (7)	0.062 (2)
C(6A)	0.4245 (2)	−0.3189 (9)	1.4133 (7)	0.068 (2)
C(7A)	0.4125 (2)	−0.2291 (9)	1.2829 (6)	0.062 (2)
C(8A)	0.3854 (2)	−0.0680 (8)	1.3097 (6)	0.051 (1)
C(9A)	0.4150 (2)	0.0595 (8)	1.3921 (6)	0.055 (2)
C(10A)	0.4397 (2)	−0.0231 (9)	1.5122 (7)	0.057 (2)
C(11A)	0.3885 (2)	0.2186 (8)	1.4280 (6)	0.059 (2)

C(12A)	0.3678 (2)	0.3037 (8)	1.3006 (6)	0.059 (2)
C(13A)	0.3383 (2)	0.1849 (8)	1.2114 (5)	0.049 (1)
C(14A)	0.3635 (2)	0.0149 (8)	1.1819 (5)	0.050 (1)
C(15A)	0.3362 (2)	−0.1111 (10)	1.0910 (6)	0.062 (2)
C(16A)	0.3080 (2)	−0.2239 (9)	1.1596 (6)	0.060 (2)
C(17A)	0.3232 (2)	0.2822 (9)	1.0841 (6)	0.057 (2)
C(18A)	0.2965 (2)	0.1457 (10)	1.2753 (6)	0.069 (2)
C(19A)	0.5250 (3)	−0.1610 (17)	1.9567 (8)	0.122 (3)
C(20A)	0.3399 (2)	0.2146 (11)	0.7866 (5)	0.062 (2)
C(21A)	0.3016 (3)	0.2015 (14)	0.7111 (7)	0.088 (3)
C(22A)	0.2913 (3)	0.0518 (15)	0.6417 (7)	0.087 (3)
C(23A)	0.3204 (3)	−0.0906 (14)	0.6502 (6)	0.084 (3)
C(24A)	0.3591 (2)	−0.0752 (12)	0.7303 (6)	0.079 (2)
C(25A)	0.3698 (2)	0.0787 (12)	0.7967 (6)	0.071 (2)
C(26A)	0.3092 (3)	−0.2570 (15)	0.5794 (7)	0.119 (3)
S(1B)	0.1635 (1)	−0.7542 (4)	1.0105 (2)	0.093 (1)
O(1B)	0.2042 (2)	−0.8351 (8)	1.0257 (5)	0.104 (2)
O(2B)	0.1255 (2)	−0.8269 (9)	0.9480 (7)	0.123 (2)
O(3B)	0.1510 (2)	−0.6933 (6)	1.1501 (4)	0.077 (1)
O(4B)	−0.0138 (2)	−0.1215 (11)	1.8494 (7)	0.127 (2)
N(1B)	0.2072 (2)	−0.0342 (8)	1.3958 (6)	0.071 (2)
C(1B)	0.0396 (2)	−0.4513 (11)	1.6642 (8)	0.076 (2)
C(2B)	0.0157 (2)	−0.3853 (12)	1.7579 (9)	0.090 (3)
C(3B)	0.0097 (2)	−0.2074 (13)	1.7609 (8)	0.083 (2)
C(4B)	0.0275 (2)	−0.1033 (12)	1.6701 (9)	0.088 (2)
C(5B)	0.0516 (2)	−0.1723 (9)	1.5760 (8)	0.069 (2)
C(6B)	0.0708 (2)	−0.0525 (10)	1.4830 (8)	0.080 (2)
C(7B)	0.0860 (2)	−0.1472 (9)	1.3630 (7)	0.068 (2)
C(8B)	0.1142 (2)	−0.3006 (8)	1.4118 (6)	0.053 (1)
C(9B)	0.0858 (2)	−0.4342 (9)	1.4736 (7)	0.061 (2)
C(10B)	0.0588 (2)	−0.3533 (9)	1.5740 (7)	0.063 (2)
C(11B)	0.1133 (2)	−0.5825 (9)	1.5316 (7)	0.072 (2)
C(12B)	0.1368 (2)	−0.6674 (9)	1.4227 (7)	0.075 (2)
C(13B)	0.1661 (2)	−0.5386 (8)	1.3580 (6)	0.057 (2)
C(14B)	0.1383 (2)	−0.3832 (8)	1.3037 (6)	0.055 (2)
C(15B)	0.1644 (2)	−0.2455 (9)	1.2318 (6)	0.064 (2)
C(16B)	0.1885 (2)	−0.1257 (9)	1.3224 (6)	0.056 (2)
C(17B)	0.1855 (2)	−0.6334 (9)	1.2463 (6)	0.061 (2)
C(18B)	0.2048 (2)	−0.4866 (9)	1.4558 (7)	0.070 (2)
C(19B)	−0.0341 (3)	−0.2306 (18)	1.9403 (11)	0.146 (4)
C(20B)	0.1700 (2)	−0.5450 (12)	0.9326 (6)	0.075 (2)
C(21B)	0.2105 (3)	−0.4944 (16)	0.9088 (8)	0.098 (3)
C(22B)	0.2147 (3)	−0.3420 (18)	0.8451 (8)	0.106 (4)
C(23B)	0.1800 (3)	−0.2318 (15)	0.8127 (6)	0.092 (3)
C(24B)	0.1398 (2)	−0.2864 (15)	0.8452 (7)	0.089 (3)
C(25B)	0.1349 (3)	−0.4430 (15)	0.9050 (8)	0.089 (3)
C(26B)	0.1842 (3)	−0.0587 (16)	0.7439 (7)	0.117 (4)

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

S(1A)—O(1A)	1.458 (7)	S(1B)—O(1B)	1.409 (7)
S(1A)—O(2A)	1.438 (6)	S(1B)—O(2B)	1.400 (7)
S(1A)—O(3A)	1.548 (5)	S(1B)—O(3B)	1.583 (5)
S(1A)—C(20A)	1.712 (8)	S(1B)—C(20B)	1.825 (9)
O(3A)—C(17A)	1.468 (7)	O(3B)—C(17B)	1.448 (8)
O(4A)—C(3A)	1.363 (10)	O(4B)—C(3B)	1.390 (10)
O(4A)—C(19A)	1.426 (12)	O(4B)—C(19B)	1.448 (14)
C(13A)—C(17A)	1.525 (8)	C(13B)—C(17B)	1.531 (9)
C(14A)—C(15A)	1.535 (9)	C(14B)—C(15B)	1.570 (9)
C(15A)—C(16A)	1.469 (10)	C(15B)—C(16B)	1.456 (9)
C(16A)—N(1A)	1.153 (9)	C(16B)—N(1B)	1.141 (9)
O(1A)—S(1A)—O(2A)	117.8 (4)	O(1B)—S(1B)—O(2B)	125.3 (4)
O(1A)—S(1A)—O(3A)	109.0 (3)	O(1B)—S(1B)—O(3B)	110.0 (7)
O(1A)—S(1A)—C(20A)	108.8 (4)	O(1B)—S(1B)—C(20B)	107.5 (4)
O(2A)—S(1A)—O(3A)	104.1 (3)	O(2B)—S(1B)—O(3B)	104.3 (4)
O(2A)—S(1A)—C(20A)	111.5 (4)	O(2B)—S(1B)—C(20B)	106.9 (4)
O(3A)—S(1A)—C(20A)	104.7 (3)	O(3B)—S(1B)—C(20B)	100.0 (3)
S(1A)—O(3A)—C(17A)	117.0 (4)	S(1B)—O(3B)—C(17B)	117.5 (4)
C(3A)—O(4A)—C(19A)	119.6 (7)	C(3B)—O(4B)—C(19B)	115.6 (8)
O(4A)—C(3A)—C(2A)	123.4 (7)	O(4B)—C(3B)—C(2B)	124.8 (8)
O(4A)—C(3A)—C(4A)	118.2 (7)	O(4B)—C(3B)—C(4B)	115.4 (7)
C(14A)—C(13A)—C(17A)	111.4 (5)	C(14B)—C(13B)—C(17B)	111.1 (5)
C(13A)—C(14A)—C(15A)	112.9 (5)	C(13B)—C(14B)—C(15B)	113.3 (5)
C(14A)—C(15A)—C(16A)	114.5 (5)	C(14B)—C(15B)—C(16B)	113.4 (5)
C(15A)—C(16A)—N(1A)	178.3 (7)	C(15B)—C(16B)—N(1B)	178.4 (7)

O(3A)—C(17A)—C(13A)	108.9 (5)	O(3B)—C(17B)—C(13B)	109.2 (5)
S(1A)—C(20A)—C(21A)	120.6 (6)	S(1B)—C(20B)—C(21B)	118.7 (6)
S(1A)—C(20A)—C(25A)	117.7 (5)	S(1B)—C(20B)—C(25B)	118.8 (6)

C(11A)—C(12A)—C(13A)—C(18A)	70.4 (6)
C(11A)—C(12A)—C(13A)—C(17A)	−175.3 (5)
C(12A)—C(13A)—C(17A)—O(3A)	57.5 (6)
C(13A)—C(17A)—O(3A)—S(1A)	165.5 (4)
C(17A)—O(3A)—S(1A)—O(1A)	45.9 (5)
C(17A)—O(3A)—S(1A)—O(2A)	172.5 (4)
C(17A)—O(3A)—S(1A)—C(20A)	−70.4 (5)
C(12A)—C(13A)—C(14A)—C(15A)	−179.3 (5)
C(13A)—C(14A)—C(15A)—C(16A)	−83.7 (7)
C(1A)—C(2A)—C(3A)—O(4A)	179.7 (7)
C(11B)—C(12B)—C(13B)—C(18B)	69.1 (7)
C(11B)—C(12B)—C(13B)—C(17B)	−176.6 (5)
C(12B)—C(13B)—C(17B)—O(3B)	59.9 (6)
C(13B)—C(17B)—O(3B)—S(1B)	165.5 (4)
C(17B)—O(3B)—S(1B)—O(1B)	34.9 (6)
C(17B)—O(3B)—S(1B)—O(2B)	171.7 (5)
C(17B)—O(3B)—S(1B)—C(20B)	−78.0 (5)
C(12B)—C(13B)—C(14B)—C(15B)	−178.4 (5)
C(13B)—C(14B)—C(15B)—C(16B)	−82.1 (7)
C(1B)—C(2B)—C(3B)—O(4B)	179.7 (8)

The corresponding bond distances, angles and torsion angles in the steroid parts of molecules A and B are in satisfactory agreement but differences between them become significant in the toluenesulfonyloxy moieties. The angle O=S=O is 125.3 (4)° in molecule B which is large compared with values of 118–121° for the corresponding angles in related compounds (Prince, Fronczek & Gandour, 1991; Pniewska & Anulewicz, 1991; Garcia, Fronczek & McLaughlin, 1991; Bachechi, Coiro, Delfini & Settimj, 1991; Ghosh, Basak, Mazumdar & Sheldrick, 1991). The S=O bond distances, which are rather long in molecule A, become significantly shorter in molecule B. This suggests the existence of two canonical forms of the sulfone moiety (March, 1977). The resonance effect in molecule A changes the character of and elongates the S=O bonds. Delocalization of the π electrons of the aromatic ring and the lone pair O(3) results in a shortening of the S—C(20) and S—O(3) bonds in molecule A. Differences between the torsion angles suggest that the orientations of the toluenesulfonyloxy moieties are slightly different in the two molecules.

The strong repulsive dipole–dipole interaction between O atoms from the SO₂ moieties and N atoms in both molecules requires the distance between them to be as large as possible and controls the conformation of these parts of the molecules. The bulky SO₂ group also influences the geometry of the C(17)—O(3) bond, which could be the reason for the absence of any estrogenic or antiestrongenic effects in this D-secoestrone derivative.

Ring-puckering coordinates (Cremer & Pople, 1975) and asymmetry parameters (Duax, Weeks & Rohrer, 1976), listed in Table 3, define the conformation of the B and C rings. The B ring exhibits a $7\alpha,8\beta$-half-chair conformation, while the C ring adopts a chair conformation.

Table 3. *Ring-puckering coordinates and asymmetry parameters*

Ring	Molecule	Q (Å)	φ (°)	θ (°)	ΔC_s (Å)	ΔC_2 (Å)	Conformation
B	A	0.548 (7)	330 (1)	130.7 (7)	—	0.9[C(7)—C(8)]	$_8H^7$
	B	0.538 (8)	330 (1)	130.8 (8)	—	0.3[C(7)—C(8)]	$_8H^7$
C	A	0.577 (6)	259 (7)	175.1 (6)	5.7[C(8)]	6.0[C(8)—C(9)]	$_9C^{13}$
					2.7[C(9)]	0.8[C(9)—C(11)]	
					3.7[C(11)]	6.5[C(11)—C(12)]	
	B	0.593 (7)	277 (9)	178.2 (7)	2.9[C(8)]	3.4[C(8)—C(9)]	$_9C^{13}$
					1.6[C(9)]	0.8[C(9)—C(11)]	
					1.8[C(11)]	3.1[C(11)—C(12)]	

Fig. 2 shows that the 3-methoxy group lies in the plane of benzene ring while the C(17)-*p*-toluenesulfonyloxy moiety is α-orientated and C(15)—C(16)≡N is β-oriented. The values of the C(1)—C(10)···C(13)—C(18) non-bonded torsion angles [-88.6 (6) and -88.9 (7)° in molecules A and B respectively] show that there is no twist along the principal axis of either molecule. The packing arrangement of the molecules indicates the existence of hydrophobic and hydrophilic layers parallel to the a axis.
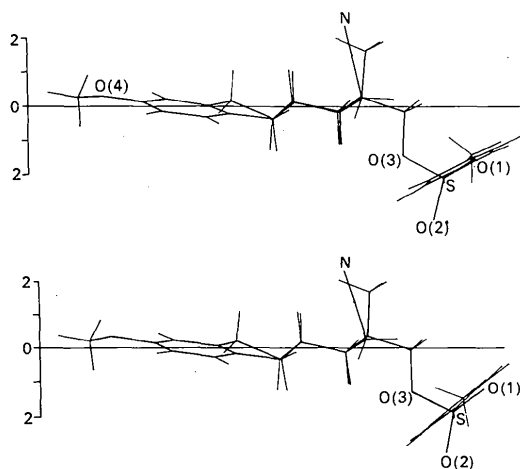
Fig. 2. The conformations of molecules A (top) and B (bottom).

Experimental

Crystal data

C₂₆H₃₁NO₄S
$M_r = 453.6$
Monoclinic
$P2_1$
$a = 31.196$ (8) Å
$b = 7.748$ (1) Å
$c = 10.154$ (2) Å
$\beta = 96.32$ (2)°
$V = 2439.4$ (8) Å³
$Z = 4$
$D_x = 1.23$ Mg m⁻³

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 22 reflections
$\theta = 15.0$-$19.5°$
$\mu = 1.33$ mm⁻¹
$T = 293$ K
Prism
$1.27 \times 0.75 \times 0.18$ mm
Colourless

Data collection

Philips PW1100 diffractometer
ω-2θ scans
Absorption correction: none
3051 measured reflections
2999 observed reflections [$F > 4.0\sigma(F)$]

$R_{int} = 0$
$\theta_{max} = 70°$
$h = -35 \rightarrow 37$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 12$
3 standard reflections frequency: 120 min intensity variation: none

Refinement

Refinement on F
Final $R = 0.057$
$wR = 0.061$
$S = 0.6$
2999 reflections
586 parameters
$w = 1.43/[\sigma^2(F) + 0.000606F^2]$

$(\Delta/\sigma)_{max} = 0.18$
$\Delta\rho_{max} = -0.31$ e Å⁻³
$\Delta\rho_{min} = 0.19$ e Å⁻³
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Program(s) used to solve structure: *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989), *UNIQUE* (Cascarano, Giacovazzo, Camalli, Spagna & Watkin, 1991). Program(s) used to refine structure: *SHELX*76. Software used to prepare material for publication: *CSU* (Vicković, 1988).

H atoms generated and refined as riding groups; overall isotropic temperature factors refined for different CH types.

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Structures of Bis(dialkylthiophosphoryl) Disulfides, [R2P(S)]2S2, R = Me, iPr, and the Question of P—S π Bonding

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Abstract

The structures of two bis(dialkylthiophosphoryl) disulfides (alkyl = methyl, isopropyl) have been determined. The torsion angles about the disulfide bonds are similar but the geometry with respect to the P—S single bonds is different, the methyl compound tending to be *trans* planar and the isopropyl analog *cis* planar. The *cisoid* geometry is associated with larger S—P—S valence angles. The drive to planarity is interpreted as a π contribution to the P—S single bond.

Comment

It was reported recently (Buranda, Gallacher & Pinkerton, 1991) that, although the torsion angle about the S—S bond in organic disulfides tends to be close to 90° with a significant energy maximum at 0 and 180°, substitution of the organic moieties by thiophosphoryl groups gives rise to a wide variety of torsion angles (values ranging from

93.6 to 180.0°). In previous literature reports on the structures of similar disulfides, [R2P(S)]2S2, the S—P—S—S torsion angles were all close to 180° (*transoid* geometry) and no unusual effects on the geometry at the P atom were noted (Lawton, 1970; Tkachev, Atovmyan & Shchepinov, 1976; Yadav, Bohra, Mehrotra, Rai & Srivastava, 1983). However, when the substituents at the P atom were cyclohexyl groups, a *cisoid* geometry (S—P—S—S torsion angle → 0°) was observed for one form, and both *cisoid* and *transoid* geometries for another (Buranda, Gallacher & Pinkerton, 1991). Thus, in the *cisoid* and *transoid* forms, the PS3 unit has a tendency to planarity. The extremely small S—P—S—S torsion angle [20.6(1)-24.7(1)°] in the *cisoid* form of the cyclohexyl compound leads to an opening of the S—P—S valence angle by about 10° with respect to the *transoid* geometry. This opening of the valence angle is evidence for an important S—S steric interaction as the molecule moves towards planarity. It was suggested that the driving force towards planarity (*cis* or *trans*) is a π interaction between filled *p* (or π) orbitals on S and empty *d* orbitals on P. As the only observation of *cisoid* geometry is for the bulky cyclohexyl substituent, we have determined the structures of two other disulfides with smaller alkyl substituents [methyl (I) and isopropyl (II)].

(I)   (II)
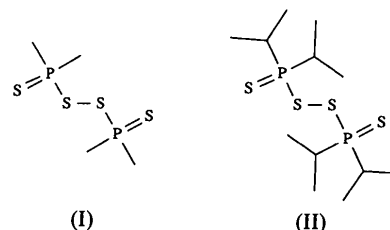
Despite the similarity between the alkyl substituents, these two disulfides fall at the two extremes of the behavior described above. The torsion angles about the disulfide bond are almost identical [(I) 113.6(1), (II) 113.47(3)°]. However, the thiophosphoryl moiety is *transoid* in the methyl compound [S—P—S—S 167.9(1), 171.2(1)°] but *cisoid* in the isopropyl analog [S—P—S—S 17.17(5), 16.35(5)°]. This difference in conformation has an important effect on the geometry at the P atom. As noted above, there is a large difference between the S—P—S valence angles in the *transoid* methyl compound [103.6(1), 103.8(1)°] compared with those in the *cisoid* isopropyl analog [115.96(4), 115.08(4)°]. The opening of the valence angle is associated with a lengthening of the P—S bond [(I) 2.100(2), 2.095(3) Å; (II) 2.1562(8), 2.1584(8) Å] and a concomitant shortening of the disulfide bond [(I) 2.074(3), (II) 2.0247(8) Å]. We note that an analogous trisulfide [Et2P(S)]2S3 also has a planar *transoid* geometry for both PS3 moieties (Gallacher & Pinkerton, 1992).

Although it is still not clear why molecules of this type should exist with a *cisoid* or *transoid* geometry, especially