

légèrement plus longue qu'une liaison Se—S simple [2,202 (2) Å dans le bis(*o*-nitrobenzenesélényle) sulfide (Eriksen, 1975)], mais elle est nettement plus courte que la somme des rayons de van der Waals de Se et S (~3,7 Å). Il y a en outre une interaction liante Se(1)···O(3) du groupe nitro. Cette distance Se···O [2,51 (1) Å] a une valeur proche de celle observée dans (II), molécule *B* [2,50 (2) Å] et correspond approximativement à la moyenne de la somme des rayons de van der Waals de S et O (~3,5 Å) et d'une liaison simple Se—O [1,774 (3) Å dans l'acide (méthylsélényle)-2 benzoïque (Dahlén, 1973)]. L'ensemble de la molécule peut être considéré comme plan. En particulier, le cycle benzène est (plan *P1*) dans la limite $1,2\sigma$. C(1) et N(1) sont également dans *P1* [distance (*d*) à *P1*, 0,015 (14) et -0,009 (15) Å, respectivement], tandis que Se(1) en est distant de -0,079 (2) Å [0,076 (1) et -0,035 (1) Å, pour (IIA) et (IIB)]. Les atomes de l'hétérocycle sont coplanaires: l'écart maximum à ce plan moyen (*P2*) concerne C(1) [$d=0,044$ (14) Å], C(3) [$d=-0,066$ (16)], C(6) [$d=-0,041$ (14)] et O(3) [$d=0,002$ (12) Å] sont très proches de *P2* tandis que O(1) s'en écarte de 0,117 (13) Å. L'angle dièdre *P1*–*P2* vaut 2,6 (1)° [1,8 (1) et 1,7 (1)° pour (IIA) et (IIB), respectivement]. (I) est donc moins plane que (II). Ceci est confirmé par les angles de torsion: valeur maxima 7 (1) contre 5 (1)° pour (II). La liaison Se(1)–C(7) est moins dissymétrique par rapport au cycle benzène que dans (II): la différence angulaire entre Se(1)–C(7)–C(2) et Se(1)–C(7)–C(6) vaut ici 3 (1)°, alors qu'elle est égale à 7 (1) et 16 (1)°,

respectivement dans (IIA) et (IIB). La même conclusion peut être faite en ce qui concerne la dissymétrie des liaisons N(1)–C(6) et C(1)–C(2): Δ entre N(1)–C(6)–C(5) et N(1)–C(6)–C(7) vaut 3 (1)°, alors que dans (IIA) et (IIB), on a respectivement, 9 (1) et 7 (1)°; quant à C(1)–C(2), les Δ correspondants sont égaux à 3 (1) (I), 12 (1) (IIA) et 14 (1)° (IIB). La cohésion du cristal est assurée uniquement par des liaisons de van der Waals. La Fig. 3 montre une vue suivant (100) de la structure.

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Structures of Two Isomeric 17-Picolinylidene* Derivatives of 5-Androsten-16-ones

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Abstract. $C_{27}H_{33}NO_3$, $M_r = 419.56$, $F(000) = 904$; *Z*-3 β -acetoxy-17-(α -picolinylidene)-5-androsten-16-

one (I), orthorhombic, $P2_12_12_1$, $a = 19.186$ (4), $b = 18.840$ (3), $c = 6.319$ (2) Å, $V = 2284$ (1) Å³, $Z = 4$, D_m (flotation) = 1.221, $D_x = 1.220$ Mg m⁻³, λ (Cu K α) = 1.54178 Å, $\mu = 5.85$ cm⁻¹, $R = 0.057$ for 1829 unique observed reflections; *E*-3 β -acetoxy-17-(α -pico-

* α -Picoline is 2-methylpyridine.

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linylidene)-5-androsten-16-one (II), monoclinic, *C*2, *a* = 28.924 (5), *b* = 6.104 (5), *c* = 13.781 (4) Å, β = 107.69 (2)°, *V* = 2318 (2) Å³, *Z* = 4, *D_m* = 1.198, *D_x* = 1.202 Mg m⁻³, $\lambda(\text{Cu K}\alpha)$ = 1.54178 Å, *R* = 0.049 for 2331 reflections. The steric difference between the two isomeric derivatives of 5-androsten-16-one is that the pyridine ring in compound (I) is in a *Z* configuration and in compound (II) an *E* configuration. The conformation of the steroid backbone is similar in both compounds and in accordance with the features of the 5-ene structures.

Introduction. In the course of our synthetic studies directed towards a partial synthesis of 21,27-hisnordemissidine and 21,27-hisnorsolamidine (Miljković, Gaši, Kindjer, Stanković, Ribár & Argay, 1985), we synthesized, as crucial intermediates, two isomeric α,β -unsaturated steroidal ketones (Fig. 1). Their structures were assumed on the basis of the chemical and spectroscopic evidence, but an exclusive proof was lacking. Therefore, in order to assign unambiguous structure and conformation to the two isomers (I) and (II), we performed the X-ray structural analysis.

Experimental.

Z-3 β -Acetoxy-17-picolinylidene-5-androsten-16-one (I)

This compound crystallizes in the shape of yellow transparent prismatic crystals. A crystal of dimensions 0.2 × 0.2 × 0.6 mm was selected for X-ray analysis and mounted on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu K α radiation (λ = 1.54178 Å). The systematic absences (*h*00: *h* = 2*n*+1, 0*k*0: *k* = 2*n*+1, 00*l*: *l* = 2*n*+1) correspond to those of the orthorhombic space group *P*2₁2₁2₁ (*Z* = 4). The refined lattice parameters *a* = 19.186 (4), *b* = 18.840 (3) and *c* = 6.319 (2) Å, were obtained by a least-squares procedure from the setting angles of 25 reflections with 10 < θ < 40°. The intensities were collected in the range 0.011 ≤ (sin θ)/ λ ≤ 0.562 Å⁻¹, ω -2 θ scan, *h* 0 to 21, *k* 0 to 21, *l* 0 to 7. Three standard reflections (060, $\bar{2}22$, $\bar{2}41$) remained constant throughout the measurement. Of 1966 independent reflections, 1829 with *F_o* > 3 σ (*F_o*) were considered as observed and used for calculations. Data were corrected for Lorentz and polarization effects but not for absorption.

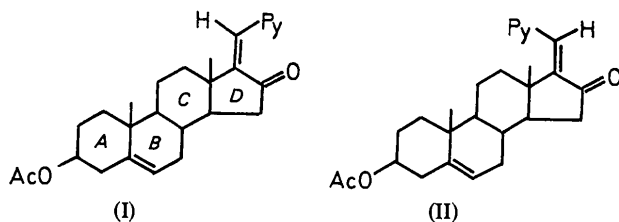


Fig. 1. Two isomers of 3 β -acetoxy-17-picolinylidene-5-androsten-16-one: (I) *Z*- and (II) *E*-.

The phase problem was solved by the direct methods *SIR* program package (Casarano, Giacovazzo, Burla, Nunzi, Polidori, Camalli, Spagna & Viterbo, 1985) using the default option with formula P10 (Casarano, Giacovazzo, Camalli, Spagna, Burla, Nunzi & Polidori, 1984) obtaining all the non-H atoms except O(1). Structure-factor and Fourier calculations revealed the position of the missing O(1) atom (*R* = 0.27). Full-matrix least-squares refinement, anisotropic for all non-H atoms, $\sum w(\Delta F^2)$ minimized, 281 parameters refined. Refinement was terminated at *R* = 0.057, *wR* = 0.069, $w = [\sigma^2(F_o) + 60 \times 10^{-4} F_o^2]^{-1}$. Max. and min. peak heights in final $\Delta\rho$ map 0.19 and -0.24 e Å⁻³. Data were not corrected for extinction. (Δ/σ)_{max} = 0.83. The H-atom positions were generated from assumed geometries and were taken into account without refinement in structure factor calculations. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Final positional parameters for non-H atoms are given with their e.s.d.'s in Table 1.*

E-3 β -Acetoxy-17-picolinylidene-5-androsten-16-one (II)

A colorless transparent crystal with dimensions 0.24 × 0.36 × 0.90 mm was used for crystallographic data collection employing the same procedure used for (I). Systematic absence *h*+*k* = 2*n* indicated that the space group was *C*2. The lattice parameters are *a* = 28.924 (5), *b* = 6.104 (5), *c* = 13.781 (4) Å, β = 107.69 (2)°, refined using 25 reflections in the range 10 < θ < 45°. Scan range: 0.011 < (sin θ)/ λ < 0.609 Å⁻¹, ω -2 θ scan, *h* -35 to 35, *k* 0 to 7, *l* 0 to 16. Three standard reflections (220, $\bar{4}21$, 512) remained constant during the measurement of 2514 reflections. Of these, 2331 with *F_o* > 3 σ (*F_o*) were considered as observed. Data were corrected for Lorentz and polarization effects. The absorption correction was also applied (Frenz & Associates Inc., 1982).

The structure was solved by direct methods using the *SHELX* program (Sheldrick, 1976) obtaining all the non-H atoms except C(23). Subsequent structure-factor and Fourier calculations gave the position of the missing C(23) atom (*R* = 0.34). Refinement was practically the same as that described for (I). The final *R* value was 0.049, *wR* = 0.066, $w = [\sigma^2(F_o) + 62 \times 10^{-4} F_o^2]^{-1}$. Max. and min. peak heights in final $\Delta\rho$ map were 0.17 and -0.19 e Å⁻³. (Δ/σ)_{max} = 0.78. The final atomic positions for non-H atoms are listed in Table 2.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, possible hydrogen bonds and interatomic van der Waals contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51440 (30 pp.) Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors of non-H atoms for compound (I)

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
N1	0.0506 (2)	0.1384 (2)	0.8032 (7)	0.059 (2)
O1	0.1856 (2)	0.0610 (2)	0.2102 (7)	0.087 (3)
O2	0.7113 (2)	0.1232 (2)	1.0244 (7)	0.069 (2)
O3	0.7048 (2)	0.0232 (2)	1.2117 (10)	0.110 (4)
C1	0.5228 (2)	0.1768 (3)	1.0150 (7)	0.052 (2)
C2	0.6002 (2)	0.1811 (3)	1.0725 (8)	0.056 (2)
C3	0.6379 (2)	0.1186 (3)	0.9723 (9)	0.059 (3)
C4	0.6305 (2)	0.1212 (3)	0.7328 (9)	0.058 (3)
C5	0.5539 (2)	0.1174 (2)	0.6741 (7)	0.046 (2)
C6	0.5308 (2)	0.0684 (2)	0.5419 (7)	0.049 (2)
C7	0.4574 (2)	0.0590 (2)	0.4743 (7)	0.046 (2)
C8	0.4126 (2)	0.1242 (2)	0.5235 (6)	0.041 (2)
C9	0.4290 (2)	0.1524 (2)	0.7490 (6)	0.040 (2)
C10	0.5062 (2)	0.1733 (2)	0.7753 (7)	0.040 (2)
C11	0.3780 (2)	0.2106 (2)	0.8167 (7)	0.048 (2)
C12	0.3003 (2)	0.1914 (2)	0.7881 (7)	0.048 (2)
C13	0.2861 (2)	0.1685 (2)	0.5616 (7)	0.042 (2)
C14	0.3353 (2)	0.1051 (2)	0.5138 (6)	0.039 (2)
C15	0.3066 (2)	0.0723 (2)	0.3116 (8)	0.050 (2)
C16	0.2285 (2)	0.0851 (3)	0.3304 (8)	0.056 (2)
C17	0.2158 (2)	0.1339 (2)	0.5173 (7)	0.045 (2)
C18	0.2944 (2)	0.2300 (2)	0.4059 (8)	0.055 (3)
C19	0.5232 (2)	0.2458 (2)	0.6748 (9)	0.055 (2)
C20	0.1591 (2)	0.1457 (2)	0.6357 (8)	0.047 (2)
C21	0.0870 (2)	0.1180 (2)	0.6334 (8)	0.049 (2)
C22	0.0570 (2)	0.0785 (2)	0.4695 (8)	0.059 (3)
C23	-0.0123 (3)	0.0610 (3)	0.4874 (10)	0.064 (3)
C24	-0.0501 (3)	0.0800 (2)	0.6595 (10)	0.064 (3)
C25	-0.0159 (2)	0.1179 (3)	0.8108 (10)	0.069 (3)
C26	0.7377 (3)	0.0720 (3)	1.1501 (9)	0.060 (3)
C27	0.8133 (3)	0.0837 (3)	1.1892 (13)	0.082 (4)

Table 2. Fractional atomic coordinates and equivalent isotropic temperature factors of non-H atoms for compound (II)

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

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
N1	0.0937 (1)	0.6420 (9)	0.1478 (2)	0.086 (2)
O1	0.1783 (1)	0.2408 (8)	-0.0715 (2)	0.082 (1)
O2	0.4856 (1)	0.6405 (6)	0.6452 (2)	0.066 (1)
O3	0.5025 (1)	0.9973 (8)	0.6355 (3)	0.113 (2)
C1	0.3556 (1)	0.7480 (8)	0.4891 (2)	0.054 (1)
C2	0.4006 (1)	0.7529 (7)	0.5834 (2)	0.058 (1)
C3	0.4430 (1)	0.6572 (7)	0.5548 (2)	0.056 (1)
C4	0.4328 (1)	0.4248 (7)	0.5161 (2)	0.059 (1)
C5	0.3865 (1)	0.4099 (6)	0.4268 (2)	0.049 (1)
C6	0.3864 (1)	0.3098 (7)	0.3422 (2)	0.056 (1)
C7	0.3431 (1)	0.2784 (7)	0.2511 (2)	0.057 (1)
C8	0.2955 (1)	0.3324 (6)	0.2722 (2)	0.044 (1)
C9	0.3016 (1)	0.5411 (6)	0.3372 (2)	0.041 (1)
C10	0.3415 (1)	0.5177 (6)	0.4419 (2)	0.044 (1)
C11	0.2530 (1)	0.6240 (7)	0.3484 (2)	0.053 (1)
C12	0.2121 (1)	0.6443 (6)	0.2469 (2)	0.050 (1)
C13	0.2051 (1)	0.4308 (6)	0.1874 (2)	0.044 (1)
C14	0.2552 (1)	0.3740 (6)	0.1729 (2)	0.045 (1)
C15	0.2440 (1)	0.2054 (7)	0.0876 (2)	0.057 (1)
C16	0.1961 (1)	0.2877 (7)	0.0179 (2)	0.059 (1)
C17	0.1741 (1)	0.4409 (7)	0.0759 (2)	0.049 (1)
C18	0.1855 (1)	0.2504 (7)	0.2422 (2)	0.057 (1)
C19	0.3241 (1)	0.3761 (7)	0.5174 (2)	0.057 (1)
C20	0.1357 (1)	0.5613 (7)	0.0265 (2)	0.059 (1)
C21	0.1069 (1)	0.7089 (8)	0.0687 (2)	0.058 (1)
C22	0.0939 (1)	0.9142 (9)	0.0223 (3)	0.076 (2)
C23	0.0662 (1)	1.0505 (9)	0.0639 (4)	0.096 (2)
C24	0.0521 (1)	0.9825 (12)	0.1432 (4)	0.102 (3)
C25	0.0663 (1)	0.7771 (13)	0.1824 (3)	0.097 (3)
C26	0.5123 (1)	0.8246 (9)	0.6759 (3)	0.071 (2)
C27	0.5554 (1)	0.7760 (12)	0.7652 (3)	0.095 (2)

Discussion. Interatomic distances and bond angles for (I) and (II) are given in Table 3. Relevant torsion angles for both molecules are presented in Fig. 2. Fig. 3 shows

Table 3. Interatomic distances (\AA) and bond angles ($^\circ$) for (I) and (II) with their e.s.d.'s in parentheses

	(I)	(II)
C(1)–C(2)	1.531 (5)	1.535 (3)
C(2)–C(3)	1.520 (7)	1.515 (5)
C(3)–C(4)	1.521 (8)	1.513 (6)
C(4)–C(5)	1.517 (6)	1.521 (3)
C(5)–C(6)	1.322 (6)	1.315 (4)
C(5)–C(10)	1.535 (6)	1.528 (5)
C(6)–C(7)	1.482 (5)	1.492 (3)
C(7)–C(8)	1.531 (5)	1.527 (4)
C(8)–C(9)	1.553 (5)	1.536 (5)
C(8)–C(14)	1.527 (5)	1.525 (3)
C(9)–C(10)	1.542 (5)	1.556 (3)
C(1)–C(10)	1.549 (6)	1.551 (6)
C(10)–C(19)	1.541 (6)	1.550 (5)
C(11)–C(9)	1.531 (5)	1.545 (4)
C(11)–C(12)	1.545 (5)	1.538 (3)
C(12)–C(13)	1.519 (6)	1.520 (5)
C(13)–C(14)	1.552 (5)	1.561 (4)
C(13)–C(18)	1.528 (6)	1.538 (5)
C(13)–C(17)	1.524 (5)	1.527 (3)
C(14)–C(15)	1.522 (6)	1.521 (5)
C(15)–C(16)	1.522 (5)	1.512 (4)
C(16)–C(17)	1.516 (7)	1.492 (5)
C(17)–C(20)	1.339 (6)	1.333 (4)
C(20)–C(21)	1.478 (5)	1.462 (5)
C(21)–C(22)	1.399 (6)	1.405 (7)
C(22)–C(23)	1.374 (7)	1.393 (7)
C(23)–C(24)	1.355 (9)	1.343 (8)
C(24)–C(25)	1.362 (8)	1.377 (10)
C(25)–N(1)	1.334 (6)	1.329 (7)
C(21)–N(1)	1.337 (6)	1.324 (5)
C(16)–O(1)	1.208 (6)	1.216 (4)
C(3)–O(2)	1.449 (5)	1.465 (3)
C(26)–O(2)	1.348 (7)	1.356 (6)
C(26)–O(3)	1.181 (7)	1.186 (7)
C(26)–C(27)	1.488 (8)	1.491 (4)
C(1)–C(2)–C(3)	108.8 (4)	108.5 (2)
C(2)–C(3)–C(4)	110.2 (4)	111.5 (3)
C(3)–C(4)–C(5)	109.4 (3)	111.8 (3)
C(4)–C(5)–C(6)	120.8 (4)	120.6 (3)
C(4)–C(5)–C(10)	116.3 (4)	116.2 (2)
C(6)–C(5)–C(10)	122.9 (4)	123.2 (3)
C(5)–C(6)–C(7)	125.7 (4)	125.5 (3)
C(6)–C(7)–C(8)	112.3 (3)	112.8 (2)
C(7)–C(8)–C(9)	110.3 (3)	109.8 (3)
C(8)–C(9)–C(10)	112.4 (3)	112.7 (3)
C(9)–C(10)–C(19)	110.6 (3)	109.6 (2)
C(9)–C(10)–C(1)	112.7 (3)	111.9 (2)
C(2)–C(1)–C(10)	115.7 (3)	114.8 (4)
C(1)–C(10)–C(5)	108.3 (3)	108.7 (3)
C(1)–C(10)–C(19)	108.8 (4)	108.8 (2)
C(1)–C(10)–C(9)	108.3 (3)	109.4 (3)
C(7)–C(8)–C(14)	110.4 (3)	110.6 (2)
C(9)–C(8)–C(14)	108.3 (3)	107.8 (3)
C(8)–C(9)–C(11)	111.8 (3)	112.5 (3)
C(10)–C(9)–C(11)	113.6 (3)	112.2 (2)
C(9)–C(11)–C(12)	114.6 (3)	114.0 (2)
C(11)–C(12)–C(13)	110.5 (3)	111.2 (3)
C(12)–C(13)–C(14)	107.0 (3)	106.4 (3)
C(13)–C(14)–C(8)	113.7 (3)	114.1 (2)
C(13)–C(14)–C(15)	104.8 (3)	105.1 (2)
C(8)–C(14)–C(15)	118.7 (3)	120.4 (3)
C(14)–C(15)–C(16)	103.1 (3)	101.8 (3)
C(15)–C(16)–C(17)	108.4 (4)	109.0 (2)
C(15)–C(16)–O(1)	124.2 (5)	126.1 (3)
C(17)–C(16)–O(1)	127.4 (4)	124.9 (3)
C(16)–C(17)–C(13)	105.1 (3)	107.3 (2)
C(17)–C(13)–C(14)	100.0 (3)	99.4 (2)
C(17)–C(13)–C(12)	116.9 (3)	116.7 (3)
C(17)–C(13)–C(18)	107.3 (3)	109.4 (3)
C(12)–C(13)–C(18)	111.9 (3)	110.9 (2)
C(13)–C(17)–C(20)	123.0 (4)	132.8 (3)
C(16)–C(17)–C(20)	131.8 (4)	119.8 (2)
C(17)–C(20)–C(21)	134.1 (4)	128.6 (3)
C(20)–C(21)–C(22)	125.4 (4)	118.3 (3)
C(21)–C(22)–C(23)	117.7 (4)	116.9 (4)
C(22)–C(23)–C(24)	121.3 (5)	120.3 (5)
C(23)–C(24)–C(25)	116.4 (5)	118.2 (4)
C(24)–C(25)–N(1)	126.0 (4)	124.3 (4)
C(25)–N(1)–C(21)	116.4 (4)	117.2 (4)
C(22)–C(21)–N(1)	122.1 (4)	123.0 (3)
C(20)–C(21)–N(1)	112.3 (4)	118.6 (3)
C(2)–C(3)–O(2)	108.8 (4)	110.1 (2)
C(4)–C(3)–O(2)	108.4 (4)	104.9 (3)

Table 3 (cont.)

	(I)	(II)
C(3)—O(2)—C(26)	117.1 (4)	117.3 (3)
O(2)—C(26)—O(3)	123.4 (5)	123.9 (4)
O(2)—C(26)—C(27)	111.0 (5)	110.3 (4)
O(3)—C(26)—C(27)	125.6 (5)	125.8 (5)

perspective views of the molecules together with the numbering scheme.

Bond distances and angles of the steroid skeleton are in agreement with those of the two isomers of 3 β -acetoxy-17,20-epoxy-17-picolyl-5-androsten-7-one (Miljković, Gaši, Kindjer, Stanković & Argay, 1987) and, consequently, with the average values for 5-ene structures (Duax, Weeks & Rohrer, 1976).

Comparing compounds (I) and (II), the main difference appears in the distances and bond angles around C(17) and C(20), which is a result of the different positions of the picolinylidene moiety. The interaction between O(1) and the pyridine ring due to the different position of the picolinylidene moiety causes, also, differences in torsion angles, which can be seen in Fig. 2. Consequently, the five-membered *D* ring in (I) adopts a half-chair conformation, while in compound (II) it exhibits a transition form between half-chair and envelope conformation, as the ring-puckering coordinates (Cremer & Pople, 1975) show (Table 4). The six-membered *A*, *B* and *C* rings have the usual conformation of 5-ene steroids. Ring *A* is in a chair conformation in both compounds. Ring *B* exhibits a transition form between the 9 α envelope (sofa) and 8 β ,9 α half-chair, while ring *C* adopts a chair conformation. The values of torsion angles C(13)—C(17)—C(20)—C(21) indicate a *Z* configuration for the picolinylidene moiety in compound (I) and an *E* configuration in compound (II).

The C(18) and C(19) methyl groups are, as usual, in β -axial positions as indicated by the C(4)—C(5)—C(10)—C(19) [70.6 (5)° for (I) and -72.0 (4)° for (II)] and C(15)—C(14)—C(13)—C(18) torsion angles [-70.5 (4)° for (I) and 74.7 (3)° for (II)]. The acetoxy moiety assumes a β -equatorial position according to the values of the torsion angles indicated in Fig. 2. The slight decrease of the O(2)—C(3)—C(4) bond angle in compound (II) and the difference in C(2)—C(3)—O(2)—C(26) torsion angles could be explained by the influence of crystal packing.

The packing arrangements looking down the *c* axis for (I) and the *b* axis for (II) are presented in Fig. 4. The molecules of compound (I) lie parallel to the *a* axis. Two molecules with equivalent positions *x*, *y*, *z* and $-x + \frac{1}{2}$, $-y$, $z + \frac{1}{2}$ are linked together by weak hydrogen bonds between O(1) and C(14) forming dimers [C(14)···O(1) = 3.390 (5) Å, H(14)···O(1) = 2.439 (5) Å, C(14)—H(14)···O(1) = 146.3 (3)°]. The interaction between molecules in compound (II), which lie almost parallel to the shorter diagonal of the *ac* plane, occurs only through van der Waals contacts.

Table 4. Ring puckering coordinates

Ring	Compound	<i>Q</i> (Å)	θ (°)	φ (°)
<i>A</i>	I	0.562 (5)	10.0 (5)	115 (3)
	II	0.545 (3)	171.4 (3)	-100 (2)
<i>B</i>	I	0.471 (4)	48.9 (5)	-150.8 (6)
	II	0.481 (4)	128.7 (5)	33.1 (6)
<i>C</i>	I	0.581 (4)	7.9 (4)	153 (3)
	II	0.580 (3)	171.9 (4)	-30 (2)
<i>D</i>	I	0.425 (4)	—	-167.7 (6)
	II	0.410 (4)	—	25.8 (5)

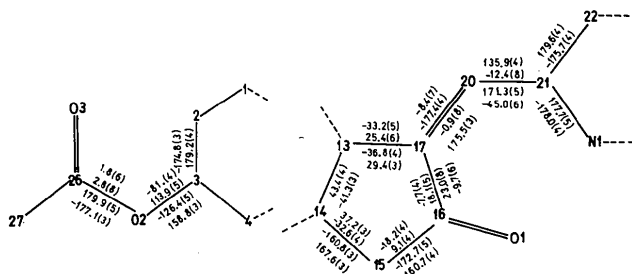


Fig. 2. Relevant torsion angles (°) for both compounds. The numbers close to the bond lines refer to molecule (I) and the others to molecule (II).

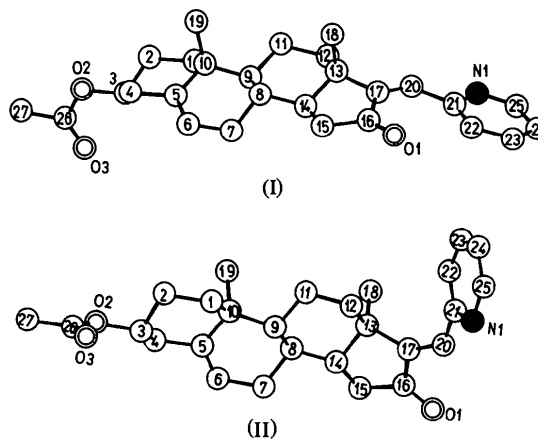


Fig. 3. Perspective views of molecules (I) and (II) showing atomic labeling. The bare numbers are for carbon atoms unless otherwise indicated.

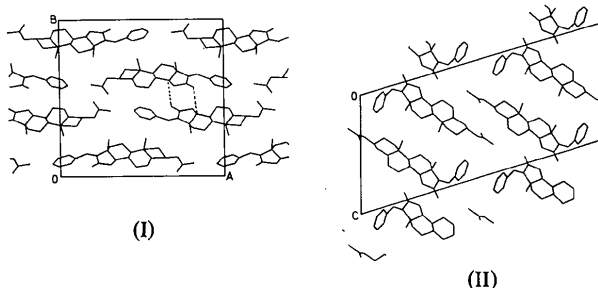


Fig. 4. The packing arrangements for both isomers looking down the *c* axis (I) and *b* axis (II). Dotted lines indicate O(1)···C(14) hydrogen bonds.

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Structure du Diméthyl-3,4 (Phényl-2 éthyl)-2 1*H*,2*H*-Thiadiazine-1,2,6 Dioxyde-1,1

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Abstract. $C_{13}H_{16}N_2O_2S$, $M_r = 264.35$, monoclinic, $P2_1/n$, $a = 7.2617$ (4), $b = 12.4524$ (6), $c = 14.7083$ (5) Å, $\beta = 89.65$ (6)°, $V = 1330.0$ (7) Å³, $Z = 4$, $D_x = 1.320$, $D_m = 1.30$ (2) Mg m⁻³, $F(000) = 1130$, $T = 295$ K, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.228$ mm⁻¹, final $R = 0.044$ for 1554 independent reflections with $I > 3\sigma(I)$. The thiadiazine ring shows a quasi-planar conformation in contrast to the folded structure usually observed in this series. This feature can be related to the presence of the bulky substituents branched on the thiadiazine ring.

Introduction. Les thiadiazines peuvent être considérés comme des analogues de la pyrimidine. Elles ont ainsi une forte potentialité pharmacologique et par conséquent leur étude structurale doit permettre une meilleure compréhension de leurs propriétés biologiques. Dans le cadre des recherches récemment entreprises dans cette série (Brouant, Pierrot, Baldy, Ochoa, Goya, Soyfer & Barbe, 1986; Brouant, Barbe, Goya & Ochoa, 1988), nous présentons ici la structure d'un composé dont l'originalité réside dans le fait que l'hétérocycle thiadiazinique est substitué par un groupement éthyl-benzène. On en trouvera la formule développée et la numérotation sur la Fig. 1.

Partie expérimentale. Cristaux prismatiques incolores obtenus par simple évaporation dans l'acétone: 0,2 × 0,2 × 0,6 mm. Densité mesurée par flottaison. Diffractomètre quatre cercles CAD-4 Enraf–Nonius avec monochromateur au graphite. Paramètres de la maille obtenus par calcul des moindres carrés sur les valeurs de $2(\sin\theta)/\lambda$ pour 23 réflexions. Intensités mesurées avec $\theta < 26^\circ$ et technique de balayage en $\theta:2\theta$. Trois réflexions de contrôle d'intensité toutes les 10000 s et trois réflexions de contrôle

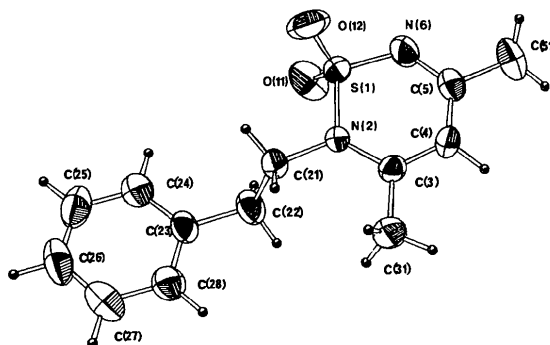


Fig. 1. Dessin en perspective de la structure cristalline avec la numérotation.