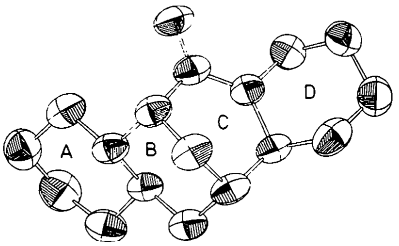

Fig. 3. *ORTEP* drawing of 17-oxosparteine.

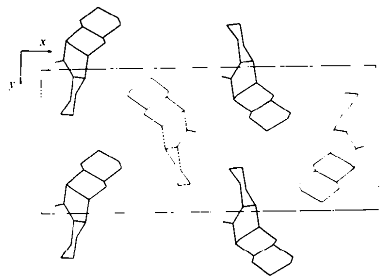

Fig. 4. Unit-cell contents and molecular packing of 17-oxosparteine.

N(16) bond distance in the lactam group is 1·350 (5) Å, and C(17)—O is 1·232 (5) Å; this indicates a slightly conjugated bond system. Similar values were obtained for the lactam group of (±)-lupanine (Doucerain, Chiaroni & Riche, 1976). The oxo substituent in the 17 position causes a greater flattening of ring *C* in the region of the lactam group than does the oxo substituent in the outer ring [in position C(2)] of (±)-lupanine (Doucerain, Chiaroni & Riche, 1976). The thermal motions of the molecule (Fig. 3) are slightly higher in comparison with those of the other sparteine derivatives (Kałuski, Skolik & Wiewiórowski, 1978); this may be connected with the rather low (351 K) melting point of the compound.

The molecular packing of 17-oxosparteine is shown in Fig. 4. There are no intermolecular contacts other than van der Waals interactions.

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Structure of *N*,*N*′-Diacetyl-3-methylthiobenzidine

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Abstract. $C_{17}H_{18}N_2O_2S$, triclinic, $P\bar{1}$, a = 9·702 (4), b = 11·027 (7), c = 7·710 (2) Å, α = 72·09 (4), β = 100·19 (3), γ = 97·18 (5)°, V = 770·3 Å^3 [at 138 (2) K] and a = 9·709 (1), b = 10·929 (2), c = 7·9983 (8) Å, α = 73·61 (2), β = 101·20 (1), γ = 98·04 (2)°, V = 795·4 Å^3, D_o = 1·316, D_c = 1·313 Mg m^{-3} (at 298 K), M_r = 314·41, Z = 2. The final R value is 0·045 for 2560 reflections. The dihedral angle between the two phenyl rings is 33·7°.

Introduction. *N*,*N*′-Diacetyl-*N*-hydroxybenzidine has been shown to be an *in vitro* metabolite of benzidine in several rodent species and may represent the proximate form of the carcinogen. The compound can be converted in hepatic cytosol to an ultimate carcinogenic electrophile, presumably *N*,*N*′-diacetyl-*N*-sulfonyloxybenzidine. The title compound is obtained when methionine is included in the sulfotransferase incubation (Morton, Beland, Evans, Hulse & Kadlubar, 1980).

Single crystals of the title compound (Fig. 1) were obtained by crystallization from ethyl acetate. A suitable crystal of size 0·43 × 0·30 × 0·19 mm was chosen for data collection. A preliminary examination

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using Weissenberg film methods indicated a triclinic lattice and the volume of the unit cell showed that there are two molecules in the unit cell (Table 1). The space group was chosen to be $P\bar{1}$ which was confirmed by the structure solution and the subsequent successful refinement of the structure. Integrated intensities of 3173 unique reflections [2637 with net $I > 2\sigma(I)$] with $2\theta \leq 53°$ for Mo $K\bar{\alpha}$ radiation (λ = 0·71069 Å) were measured using the θ–2θ scan technique at 138 (2) K on a Nonius CAD-4 diffractometer equipped with an Enraf–Nonius cold-stream cooling device. The scan and aperture widths were (1 + 0·2 tan θ)° and (4 + 0·86 tan θ) mm respectively. A maximum of 60 s was spent on each reflection (40 s for scanning the peak and 10 s for scanning each of the left and right backgrounds). The intensities of three monitor reflections, measured after every 3000 s of X-ray exposure, showed a maximum variation of ±1%. The orientation matrix was checked after every 300 measurements. Lorentz and polarization corrections were applied to individual structure amplitudes but no absorption correction was made (μ = 0·21 mm^{-1}). An experimental weight based on counting statistics was applied to each structure amplitude (Ealick, van der Helm & Weinheimer, 1975).

The structure was solved by direct methods using the computer program *MULTAN* (Germain, Main & Woolfson, 1971) which yielded all S, C, N and O atoms. The structure was refined by a block-diagonal least-squares method and, after several cycles of refinement, a difference Fourier map was calculated which showed the positions of all the H atoms. The structure was further refined with anisotropic thermal parameters for the non-hydrogen atoms and isotropic temperature factors for the H atoms. The R factor, (= $\sum||kF_o| - |F_c||/\sum|kF_o|$) based on final parameters (Table 2),* was 0·045 for 2560 reflections (0·061 for all reflections). At this stage, all shifts were less than 0·25σ. The scattering factors for S, C, N and O atoms were taken from *International Tables for X-ray Crystallography* (1962) while those for H were taken from Stewart, Davidson & Simpson (1965).

Discussion. The molecule consists of two phenyl rings, two *N*-acetyl groups and a SCH$_3$ substituent on one of

Table 1. *Working cell and reduced cell*

Original cell (triclinic)	Reduced cell (triclinic)
a = 9·702 Å	a = 13·747 Å
b = 11·027	b = 11·347
c = 7·710	c = 7·710
α = 72·09°	α = 112·37°
β = 100·19	β = 97·00
γ = 97·18	γ = 127·66
V = 770·3 Å^3	V = 770·3 Å^3

Matrix for conversion to reduced cell:

$$\begin{bmatrix} 1 & 1 & 0 \\ 0 & -1 & 1 \\ 0 & 0 & -1 \end{bmatrix}.$$

Matrix for conversion of atomic coordinates for reduced cell:

$$\begin{bmatrix} 1 & 1 & 1 \\ 0 & -1 & -1 \\ 0 & 0 & -1 \end{bmatrix}.$$

Table 2. *Positional parameters* (×10^5) *and* U_{eq} (×10^4) *of non-hydrogen atoms*

The standard deviations for the last digits are given in parentheses.

	x	y	z	U_{eq} (Å^2)*
C(1)	74605 (19)	95958 (17)	42844 (23)	173 (11)
C(2)	80972 (19)	84431 (18)	48253 (28)	182 (11)
C(3)	80130 (19)	77031 (18)	36340 (29)	186 (11)
C(4)	73001 (19)	81405 (18)	18385 (28)	174 (11)
C(5)	66525 (20)	92751 (18)	12974 (28)	189 (11)
C(6)	67270 (20)	99939 (18)	25053 (29)	190 (11)
N(7)	72866 (16)	74413 (15)	5501 (23)	183 (9)
C(8)	61103 (20)	69793 (18)	−3080 (28)	193 (11)
C(9)	63032 (21)	62997 (20)	−16557 (30)	244 (12)
O(10)	49290 (14)	70900 (15)	−114 (24)	328 (11)
S(11)	88541 (6)	62538 (5)	43740 (9)	307 (3)
C(12)	73461 (27)	51085 (21)	45667 (35)	357 (15)
C(1)'	75632 (19)	103774 (17)	55840 (27)	170 (11)
C(2)'	87425 (19)	103933 (18)	69050 (29)	197 (11)
C(3)'	88582 (19)	111302 (18)	81064 (29)	194 (11)
C(4)'	77642 (19)	118707 (17)	80088 (29)	171 (11)
C(5)'	65676 (19)	118513 (18)	67129 (29)	188 (11)
C(6)'	64710 (20)	111218 (18)	55104 (29)	192 (11)
N(7)'	77652 (16)	126098 (15)	92207 (23)	180 (10)
C(8)'	88514 (20)	129563 (17)	103814 (29)	205 (11)
C(9)'	84636 (22)	136689 (24)	115740 (34)	316 (15)
O(10)'	100747 (14)	127081 (15)	104884 (22)	302 (10)

* $U_{eq} = (1/6\pi^2)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

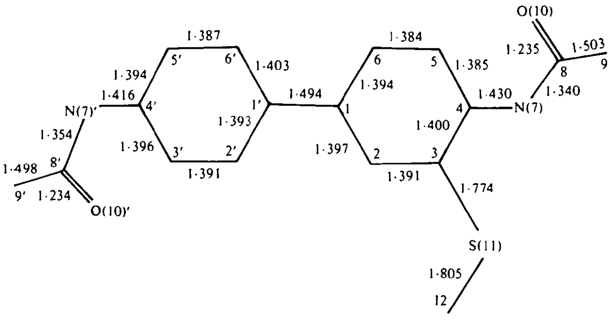

Fig. 1. Bond distances (Å). Standard deviations are 0·003 Å.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35308 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the phenyl rings. The aromatic C—C distances are normal and vary from 1·384 to 1·403 Å with mean values of 1·392 and 1·394 Å respectively for the two phenyl rings. The mean endocyclic angles for both rings are 120·0°. Observations have been made in the case of biphenyl, *p,p′*-bitolyl and 2*H*-nonafluorobiphenyl (Charbonneau & Delugeard, 1976; Casalone, Marioni, Mugnoli & Simonetta, 1969; Hamor & Hamor, 1978) that the endocyclic angles lying on the long molecular axis are slightly smaller than 120° while the other endocyclic angles are slightly greater than 120°. The present structure shows a similar trend with angles at C(1), C(4), C(1)′ and C(4)′ being 118·3, 119·8, 117·8 and 119·3° respectively (Fig. 2). The other endocyclic angles are greater than 120° with the exception of angles at C(3) and C(3)′ (119·1 and 119·6°). The C(1)—C(1)′ bond length is 1·494 Å. This is 1·496 in biphenyl, 1·478 and 1·487 in 4,4′-dichlorobiphenyl (Brock, Kuo & Levy, 1978) and 1·486 Å in 2*H*-nonafluorobiphenyl. The apparent shortening of the C(1)—C(1)′ bond in the last three cases is probably due to high thermal vibration as the data for those structures were taken at room temperature. The two S—C bond lengths C(3)—S(11) and C(12)—S(11) are 1·774 and 1·805 Å. This difference is expected because of sp^2 and sp^3 hybridization at C(3) and C(12) respectively. The C—N bonds involving the acetyl C are 1·340 and 1·354 Å. This is 1·353 in 2-acetamido-2,3-dideoxy-D-*erythro*-hex-2-enono-1,4-lactone (Ružić-Toroš & Lazarini, 1978), 1·328 in *N*-acetyl-L-tyrosine-*p*-nitroanilide (Michel & Durant, 1976) and 1·325 Å in small peptides (Marsh & Donohue, 1967). The C(4)—N(7) and C(4)′—N(7)′ bond lengths are 1·430 and 1·416 Å respectively (1·455 Å in peptides). The C(4)—N(7) and C(4)′—N(7)′ bond lengths would be expected to be slightly shorter than those in peptides because of sp^2 hybridization of atoms C(4) and C(4)′. The angle at N(7) is 123·8° and at N(7)′ is 128·8°. The N—H bond lengths are 0·842 and 0·848 Å and the C—H bond lengths vary from 0·918 to 1·064 Å.

The two acetyl groups lie in opposite directions across the long molecular axis. The planarity of the *N*-acetyl groups is described by the parameters χ_C, χ_N and τ which are functions of the torsion angles ω_1, ω_2, ω_3 and ω_4 as defined by Winkler & Dunitz (1971). χ_C for both the *N*-acetyl groups are very close to zero (0·6 and 0·5°) and indicate that out-of-plane bending at C(8) and C(8)′ is negligible whereas χ_N values are −4·3 and −4·6° indicating a slight out-of-plane bending at N(7) and N(7)′. The torsion angles of the *N*-acetyl groups and the SCH_3 group are given in Table 3.

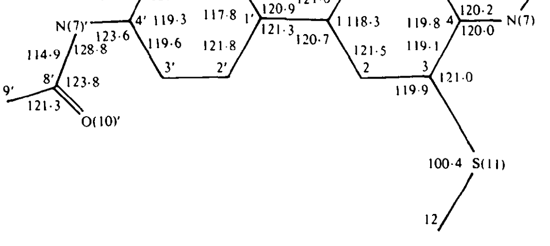

Fig. 2. Bond angles (°). Standard deviations are 0·2°.

Table 3. *Torsion angles in the N-acetyl groups and* SCH_3 *group*

The standard deviations of the conformational angles and χ_C are 0·3°. For χ_N and τ the standard deviations are 0·9°.

C(3)—C(4)—N(7)—C(8)	122·3°	14·7°
C(5)—C(4)—N(7)—C(8)	−60·1	−168·3
C(2)—C(3)—S(11)—C(12)	109·4	
C(4)—C(3)—S(11)—C(12)	−72·8	
χ_C $(= \omega_1 - \omega_3 + \pi)$	0·6	0·5
χ_N $(= \omega_2 - \omega_3 + \pi)$	−4·3	−4·6
τ $[= \frac{1}{2}(\omega_1 + \omega_2)]$	176	181·6

Table 4. *Least-squares planes and deviations* (Å)

Plane I: $8{\cdot}200x + 3{\cdot}362y - 2{\cdot}554z = 8{\cdot}243$
Plane II: $4{\cdot}330x + 5{\cdot}926y - 4{\cdot}004z = 7{\cdot}184$

Plane I	Δ	Plane II	Δ
C(1)*	0·006 (3)	C(1)′*	0·004 (3)
C(2)*	0·003 (4)	C(2)′*	−0·005 (4)
C(3)*	−0·011 (4)	C(3)′*	0·001 (4)
C(4)*	0·010 (4)	C(4)′*	0·005 (3)
C(5)*	−0·001 (4)	C(5)′*	−0·006 (4)
C(6)*	−0·007 (4)	C(6)′*	0·002 (4)
S(11)	0·003 (1)	N(7)′	−0·042 (3)
C(12)	−1·668 (4)	C(8)′	0·169 (4)
N(7)	0·093 (3)	C(1)	0·017 (3)
C(8)	−0·808 (4)		
C(1)′	0·021 (3)		

* Atoms used in the calculation of the least-squares planes.

The least-squares planes of the two phenyl groups are given in Table 4. The two phenyl rings are planar. The acetyl groups are rotated out of the respective phenyl rings, as indicated by the deviations of atoms C(8) and C(8)′ (Table 4). The dihedral angle between the two phenyl rings is 33·7°. This is smaller than the dihedral angles found in 4,4′-dichlorobiphenyl (39·4°) and pentafluorobiphenyl (52·9°) (Brock, Naae, Goodhand & Hamor, 1978).

A packing drawing is shown in Fig. 3. All O and N atoms take part in hydrogen-bond formation. N(7) donates a hydrogen bond to O(10)′(2 − *x*, 2 − *y*, 1 − *z*) with dimensions: N···O 2·852, H···O 2·03 Å and N—H···O 165·5°. N(7)′ donates a hydrogen bond to O(10)(1 − *x*, 2 − *y*, 1 − *z*) with dimensions: N···O 2·867, H···O 2·04 Å and N—H···O 161·5°. Two S atoms (*x*,*y*,*z* and 2 − *x*, 1 − *y*, 1 − *z*) approach each other at a distance of 3·558 Å, slightly larger than the sum of their van der Waals radii (van der Helm, Lessor

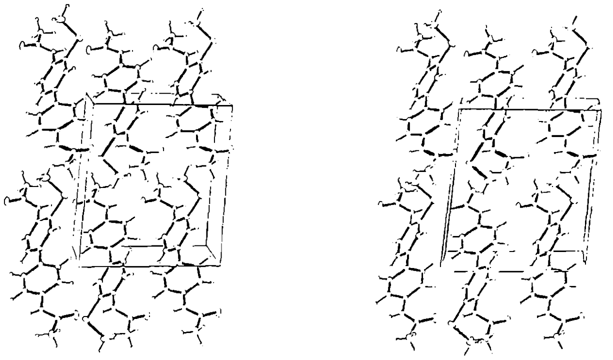

Fig. 3. *ORTEP* packing drawing and intermolecular hydrogen bonding (Johnson, 1965).

& Merritt, 1962). The hydrogen bonding may be responsible for the differences in the dimensions of the two *N*-acetyl groups in the molecule.

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Structure of the 4-Nitroguaiacyl Ester of *N*-Benzyloxycarbonyl-L-isoleucine

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Abstract. $C_{21}H_{24}N_2O_7$, $M_r = 416{\cdot}42$, monoclinic, $P2_1$, $a = 19{\cdot}433\ (3)$, $b = 5{\cdot}143\ (2)$, $c = 10{\cdot}926\ (3)$ Å, $\beta = 104{\cdot}30\ (2)°$, $V = 1058{\cdot}2$ Å^3, $Z = 2$, $D_m = 1{\cdot}30$ Mg m^{-3}, $F(000) = 440$, μ(Cu $K\alpha$) = 0·74 mm^{-1}. The structure was solved by direct methods and refined by the full-matrix least-squares procedure to $R = 0{\cdot}060$ and $R_w = 0{\cdot}044$ for 1443 F_o values obtained by a combination of two independent measurements. The molecule exists in a bow-like form with aromatic rings at the ends lying nearly perpendicular one to another. The torsion angles φ and ψ are 86·7 (5) and −146·3 (3)°, respectively.

Introduction. 4-Nitroguaiacyl esters of amino acids have been proposed (Bankowski & Drabarek, 1971) as acylating agents in peptide synthesis. It was found that 4-nitroguaiacyl esters of N-protected amino acids react faster than *p*-nitrophenyl esters and the danger of racemization at the chiral center is then lowered. As an attempt to elucidate the racemization stability of 4-nitroguaiacyl esters, the formation of an intramolecular hydrogen bond between the methoxy group in the *ortho* position and the H atom at C(6) was postulated (Bankowski & Drabarek, 1972; Bankowski, Lipkowski & Drabarek, 1974). Since it was impossible