

in triazolopyrazine respectively]. The dihedral angle between triazolotetrazine and the phenyl ring is close to 0° [$1.4(6)^\circ$], indicating attractive interactions $H(C11)\cdots N(5)$ of $2.45(5) \text{ \AA}$ [$\angle H(C11) = 97(3)^\circ$] and $H(C15)\cdots N(7)$ of $2.43(5) \text{ \AA}$ [$\angle H(C15) = 99(4)^\circ$] (Taylor & Kennard, 1982) as well as the partial double-bond character between sp^2 -hybridized N and C atoms [$N(6)-C(10)$ distance is $1.444(7) \text{ \AA}$].

Intermolecular hydrogen bonds and unusual short non-bonded contacts are not observed.

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Structure of 3-Acetoxyindole

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Abstract. Indol-3-yl acetate, $C_{10}H_9NO_2$, $M_r = 175.2$, monoclinic, $P2_1/c$, $a = 6.777(2)$, $b = 8.706(3)$, $c = 15.375(4) \text{ \AA}$, $\beta = 96.02(2)^\circ$, $V = 902.1(2) \text{ \AA}^3$, $Z = 4$, $D_m = 1.29$, $D_x = 1.290 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$, $\mu = 0.850 \text{ cm}^{-1}$, $F(000) = 368$, $T = 296 \text{ K}$, $R = 0.065$ for 1117 observed reflections. The indole system and acetoxy group are almost planar, and the acetoxy group makes a dihedral angle of 66.1° with the pyrrole ring. The crystal structure is stabilized by an $N-H\cdots O$ hydrogen bond [$N1-O2 = 2.849(2) \text{ \AA}$ and $\angle N1-H\cdots O2 = 177^\circ$].

Introduction. The study of indole derivatives is important in the history of organic chemistry, due to their varied biological, chemical and pharmacological properties. The title compound is structurally similar to the important derivative, 3-indoleacetic acid which is a plant growth hormone. As an aid to understanding its biological and pharmacological significance, and to provide further structural data on substituted indoles, we have investigated the solid-state structure of the title compound by X-ray diffraction methods.

Experimental. Single crystals obtained by slow evaporation of the powdered substance in ether-petrol (1:3). The approximate dimensions of the selected specimen were $0.2 \times 0.3 \times 0.175 \text{ mm}$. Inten-

sities measured by $\omega-2\theta$ scan method, $0 \leq 2\theta \leq 50^\circ$, using a $P2_1$ diffractometer with $\text{Mo } K\alpha$ radiation. Density measured by flotation in aqueous KI solution. Unit-cell constants derived by least-squares analysis of 25 reflections for which $25^\circ < 2\theta < 35^\circ$. Range of h,k,l : $h = 0 \rightarrow 8$, $k = 0 \rightarrow 11$, $l = -19 \rightarrow 19$. Out of 1850 unique reflections, 1117 had intensities greater than $2\sigma(I)$ and were used in the subsequent analysis. Lorentz and polarization corrections were applied but no absorption or extinction corrections were made.

The structure was solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Refinement carried out first with isotropic temperature factors and then with anisotropic temperature factors for non-H atoms. H atoms associated with the benzene ring were generated geometrically. Other H atoms located from the difference map and given the same isotropic temperature factors as the atoms to which they were bonded. H-atom positions were not refined. The final $R = 0.065$ and $wR = 0.061$ with 118 parameters. $\sum w(\Delta F)^2$ minimized with weighting factor $w = 1/\sigma^2(F_o)$, S (goodness of fit) = 0.65, $(\Delta/\sigma)_{\text{max}} = 0.55$ and $(\Delta/\sigma)_{\text{mean}} = 0.31$. Maximum and minimum heights in final difference map were within $\pm 0.5 e \text{ \AA}^{-3}$. The non-hydrogen scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) and for H atoms from Stewart, Davidson & Simpson (1965).

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Computations were carried out on a Burroughs B6700 computer system (Regional Computer Centre, Calcutta) with modified programs from *XRAY ARC* (Vickery, Bright & Mallinson, 1973).

Discussion. The atomic coordinates, bond lengths, bond angles and selected torsion angles are listed in Tables 1 and 2.* A projection of the structure onto the *bc* plane is shown in Fig. 1. Bond lengths and bond angles agree with those in related compounds (e.g. Chakraborty & Talapatra, 1986; Yamaguchi, Iitaka, Shudo & Ikamoto, 1980; Pasternak, 1956).

In the five-membered ring of the molecule the two N—C bonds are shortened compared to the normal value of 1.47 Å (Sutton, 1965). The further shortening of N1—C9 [1.377 (5) Å] with respect to N1—C2 [1.428 (5) Å] is due to extension of delocalization of the aromatic ring (Bocelli & Rizzoli, 1989). This type of shortening is also found in a skatole complex (Hanson, 1964), 3-benzyl-2-methylindole (Chakraborty & Talapatra, 1986) and other indole derivatives (Yagamuchi, Iitaka, Shudo & Ikamoto, 1980; Ishida, Yamashita, Takai & Inoue, 1983; Dewar & Gleicher, 1966). The C2—C3 double bond [1.342 (6) Å] is identical to the corresponding bond in 3-indoleacetic acid (Karle, Britts & Gum, 1964). The two C—O bonds in the acetoxy group are 1.355 (5) and 1.203 (5) Å, compared to 1.298 and 1.223 Å in 3-indoleacetic acid.

The indole nucleus is planar within the limits of experimental error.

The dihedral angle between the benzene and pyrrole rings of the indole system is 1.8 (5)°. The atom N1 is out of plane by 0.014 (3) Å. The mean plane through the atoms O1, C10, C11 makes a dihedral angle of 66.1 (5)° with the pyrrole ring plane. The acetoxy group is also planar having a torsion angle C3—O1—C10—C11 = 179.2 (5)°. The NH group of the five-membered ring is engaged in an intermolecular hydrogen bond with the carbonyl

* Lists of structure factors, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53281 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

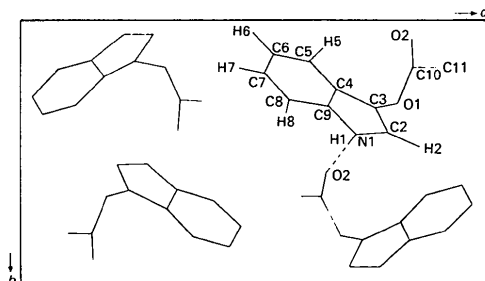


Fig. 1. Projection of the structure onto the *bc* plane.

Table 1. Fractional atomic coordinates ($\times 10^4$) with e.s.d.'s and equivalent isotropic thermal parameters

$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{Å}^2)$
O1	5625 (4)	3212 (3)	8105 (2)	4.6
O2	6455 (4)	760 (3)	8399 (2)	5.8
N1	10146 (5)	4426 (4)	7245 (2)	4.1
C2	8756 (6)	4410 (5)	7882 (2)	4.4
C3	7299 (6)	3404 (4)	7643 (2)	3.8
C4	7617 (6)	2738 (4)	6821 (2)	3.3
C5	6608 (6)	1685 (5)	6251 (2)	4.1
C6	7398 (7)	1349 (5)	5477 (3)	4.9
C7	9168 (7)	2063 (5)	5270 (2)	4.9
C8	10203 (6)	3094 (5)	5813 (2)	4.2
C9	9418 (6)	3420 (4)	6599 (2)	3.4
C10	5349 (6)	1823 (4)	8470 (2)	4.0
C11	3521 (7)	1809 (5)	8950 (3)	6.0

Table 2. Bond lengths (Å), angles (°) and selected torsion angles (°)

E.s.d.'s for the torsion angles are ca 0.4–0.6°.

C3—O1	1.410 (5)	C4—C9	1.430 (5)
O1—C10	1.355 (5)	C5—C6	1.387 (6)
N1—C2	1.428 (5)	C6—C7	1.417 (6)
N1—C9	1.377 (5)	C7—C8	1.368 (6)
C2—C3	1.342 (6)	C8—C9	1.399 (5)
C3—C4	1.426 (5)	C10—C11	1.506 (6)
C4—C5	1.397 (5)	C10—O2	1.203 (5)
C3—O1—C10	117.9 (3)	C6—C7—C8	122.9 (4)
C2—N1—C9	106.1 (3)	C5—C4—C9	119.8 (3)
N1—C2—C3	109.7 (3)	C7—C8—C9	116.3 (4)
O1—C3—C2	123.1 (3)	N1—C9—C4	110.0 (3)
O1—C3—C4	127.0 (3)	N1—C9—C8	127.8 (3)
C3—C4—C5	135.5 (4)	C4—C9—C8	122.2 (3)
C3—C4—C9	104.7 (3)	O1—C10—O2	122.3 (4)
C4—C5—C6	118.0 (4)	O1—C10—C11	111.5 (3)
C5—C6—C7	120.8 (4)	O2—C10—C11	126.2 (4)
N1—C2—C3—C4	−1.8	C3—O1—C10—C11	179.2
N1—C2—C3—O1	−175.1	C3—O1—C10—O2	−1.4
C2—C3—C4—C9	1.0	C4—C9—N1—C2	−1.3
C2—C3—O1—C10	−117.6	C4—C5—C6—C7	−0.4
C3—C4—C9—N1	0.2	C4—C3—O1—C10	70.4
C3—C4—C5—C6	178.3		

moiety having N1—O2 = 2.849 (2) Å and \angle N1—H1...O2 = 177°. There are no unusually short intermolecular contacts.

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Structure of (+)-[S-(E)]-N-(α -Methylbenzylidene)-*p*-toluenesulfinamide

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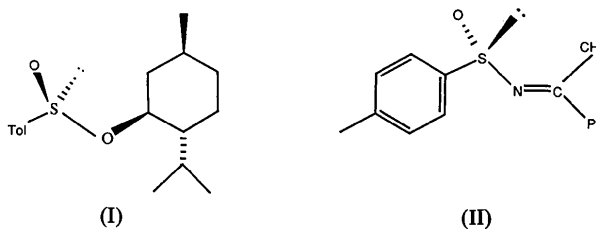
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Abstract. C₁₅H₁₅NOS, *M_r* = 257.35, monoclinic, *P*2₁, *a* = 7.710 (2), *b* = 5.903 (5), *c* = 14.700 (3) Å, β = 91.48 (2)°, *V* = 668.8 (6) Å³, *Z* = 2, *D_x* = 1.278 g cm⁻³, λ (Mo *K* α) = 0.71069 Å, μ = 2.18 cm⁻¹, *F*(000) = 272, *T* = 296 K, *R* = 0.043, 944 unique observed reflections. This is the first structure determination of an *N*-alkylidenesulfinamide. The C=N bond is distorted and lengthened presumably because of the steric interaction and electron-withdrawing effect of the sulfinyl group. The non-planar conformation is also a result of repulsive steric interaction. The configuration at C=N is *trans*. The title compound was obtained from the displacement reaction of (–)-1-menthyl (*S*)-*p*-toluenesulfinate with methyllithium.

Introduction. We have recently studied some asymmetric reactions of chiral *N*-alkylidenesulfinamides. Their preparation as reported (Cinquini & Cozzi, 1977*a*) involved the reaction of an alkyl or aryl Grignard reagent with benzonitrile and subsequent reaction with (–)-1-menthyl (*S*)-*p*-toluenesulfinate (I). However, the yields were low and the stereochemistry at C=N of the *N*-alkylidenesulfinamides was not reported. We found that treatment of methylmagnesium bromide with benzonitrile followed by sulfinate (I) gave only 12% yield of (+)-[S-(E)]-N-(α -methylbenzylidene)-*p*-toluenesulfinamide (II). The use of methyllithium instead of methylmagnesium

bromide increased the yield to 50%. The relative stereochemistry at the S site and C=N of (II) was determined by this X-ray study. The absolute configuration at the S site is assigned the *S* configuration based on studies by Cinquini & Cozzi (1977*a*). This determination of the stereochemistry at C=N in turn provides explanations for the stereochemical course followed in the asymmetric transformations of chiral *N*-alkylidenesulfinamides (Cinquini & Cozzi, 1977*b*; Hua, Miao, Chen & Saha, 1990). Chelation of the O atom with metal hydride directs the attack from the pre-*S* face of the C=N.



Experimental. Compound (II) displayed satisfactory ¹H NMR (400 MHz), ¹³C NMR (100 MHz), UV, IR and low-resolution mass spectra (both EI and CI) and satisfactory elemental analysis. Title compound, (+)-[S-(E)]-N-(α -methylbenzylidene)-*p*-toluenesulfinamide (II), was prepared as follows. To a cold (273 K) solution of 1.75 g (17 mmol) benzonitrile in 20 ml ether under argon was added a solution of 11.8 ml (17 mmol) methyllithium (1.5 M in ether). Solution stirred at 173 K for 1 h, cold (273 K) solution of (I) (2.5 g, 8.5 mmol) added. After stirring at

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