

(IVA)	10.6 (5)	5.0 (5)	52.3 (6)	332.1 (7)
(IVB)	6.1 (5)	4.6 (5)	52.4 (6)	332.4 (8)
(IVC)	8.7 (6)	5.0 (5)	50.0 (6)	331.2 (8)

For compound (I), the data collection included the measurement of the Friedel mates of all reflections within the listed *hkl* range. For each compound, the H atoms were located in a difference electron-density map and for compounds (I) and (III), they were refined isotropically. For (II) and (IV), the positions were geometrically optimized and held fixed (C—H = 0.95 Å), while the isotropic displacement parameters of (II) were refined and those of (IV) were fixed at $1.2U_{eq}$ of the parent C atom.

MSC/AFC *Diffraction Control Software* (Molecular Structure Corporation, 1991) was used for data collection and cell determination, and *TEXSAN* (Molecular Structure Corporation, 1989) was used for data reduction, structure refinement and the preparation of publication material. The structures were solved using direct methods (*SHELXS86*; Sheldrick, 1990) and the molecular graphics were produced using *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including torsion angles and contact distances, together with 50% displacement ellipsoid plots of the B and C molecules of compound (IV) have been deposited with the IUCr (Reference: AB1372). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Hexanoyl-1-tosylindole. A Highly Stereospecific Preparation of 3-Alkyl-Substituted Indoles

SOAD MOHIALDIN-KHAFFAF, KRISHNA C. PERSAUD AND ROBIN G. PRITCHARD*

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England. E-mail: robin.pritchard@umist.ac.uk

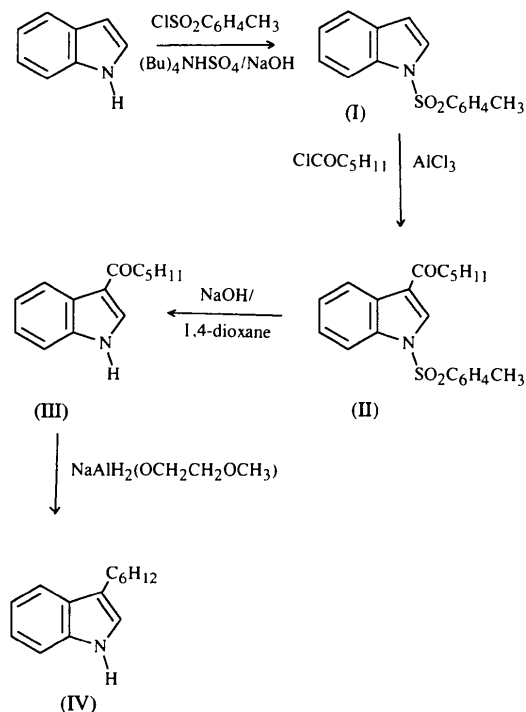
(Received 23 January 1995; accepted 3 May 1996)

Abstract

The title molecule, 1-(1-tosyl-3-indolyl)-1-hexanone, $C_{21}H_{23}NO_3S$, is configured so that the indole moiety eclipses one sulfonyl O atom and the toluene ring the other. As expected, the hexanoyl O atom is almost coplanar with the delocalized indole system.

Comment

3-Alkylindoles carrying an alkyl substituent larger than ethyl were previously unknown. We therefore synthesized 3-hexylindole, (IV), via Friedel–Craft acylation of 1-tosylindole, (I), which gave 3-hexanoyl-1-tosylindole, (II), as an intermediate. This was followed by saponification of the tosyl group and reduction of the ketone. The high yield of 3-hexanoyl-1-tosylindole and



the absence of any 2- or 5-substituted product results from the attacking electrophile being directed into the 3-position by both electronic and steric means. Activation of electrophilic substitution by the indole N atom is most marked in the five-membered ring but the bulky tosyl group masks the 2-position.

The crystal structure of the acyl intermediate (II), determined in order to confirm the reactions proposed above, shows the molecule is configured so that the indole moiety eclipses one sulfonyl O atom [O2—S1—N1—C2 $-2.7(4)^\circ$] and the toluene ring the other [O3—S1—C16—C17 $-3.7(6)^\circ$] (Fig. 1). This contrasts with the situation in 1-phenylsulfonylindole and related compounds (Beddoes, Dalton, Joule, Mills, Street & Watt, 1986) where lines drawn perpendicular to the ring planes bisect the O—S—O angle. As expected, the acetyl substituent lies in the indole plane [O1=C10—C3—C4 $2.2(6)^\circ$].

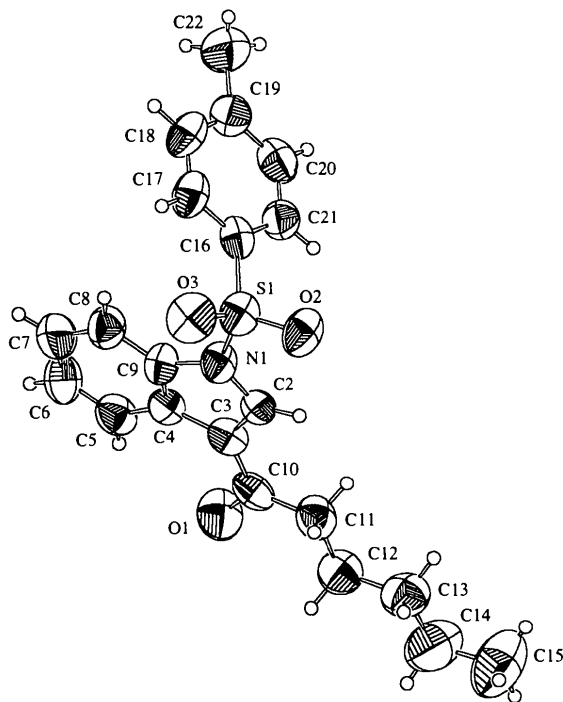


Fig. 1. An ORTEP (Johnson, 1976) plot of the title molecule showing the atomic numbering scheme and with ellipsoids drawn at the 50% probability level.

The five-membered ring in the title structure displays a typically high degree of delocalization, with C2—C3 and N1—C2 distances of 1.364 (8) and 1.379 (8) Å, respectively. This is in contrast to the formal representation of localized double C=C and single S—N bonds, a form which is only rarely encountered in actual molecules. One such case is 1-acetylkatole (Surcouf, Mornon & Malgrange, 1978) with C=C and N—C distances of 1.339 (5) and 1.406 (5) Å, respectively, where the N atom is conjugated with an exocyclic acetyl substituent.

Experimental

Aluminium trichloride (6.01 g, 45.2 mmol) was suspended in dichloromethane (80 ml) under nitrogen. A solution of hexanoyl chloride (6.62 g, 49.2 mmol) in dichloromethane (20 ml) was added slowly to the stirred mixture at ambient temperature. After the addition was complete, the mixture was stirred for a further 10 min and cooled to 278 K. *N*-Tosylindole (45.2 mmol, 12.24 g) in dichloromethane (20 ml) was added to the mixture while the temperature was kept at 278 K. After stirring at room temperature for a further 2 h, the reaction mixture was treated with ice water, extracted with dichloromethane and dried over magnesium sulfate. Evaporation of the solvent gave a thick oil which crystallized in the presence of methanol and dichloromethane to give colourless crystals of 3-hexanoyl-1-tosylindole (13.07 g, 35.42 mmol, 78%). M.p. 364–366 K; analysis found: C 68.1, H 6.1, N 3.8, S 8.5%; C₂₁H₂₃NO₃S requires: C 68.3, H 6.2, N 3.8, S 8.6%; ¹H NMR (CDCl₃/TMS, 300 MHz): 0.93 (*t*, 3H), 1.38 (*m*, 4H), 1.76 (*m*, 2H), 2.36 (*s*, 3H, Me in tosyl), 2.86 (*t*, 2H), 7.25 (*d*, 2H, Ar in tosyl), 7.35 (*m*, 2H, indole), 7.81 (*d*, 2H, Ar in tosyl), 7.92 (*dm*, 1H), 8.21 (*s*, 1H, indole), 8.35 p.p.m. (*dm*, 1H, indole).

Crystal data

C₂₁H₂₃NO₃S
M_r = 369.47
 Monoclinic
*P*2₁/*n*
a = 8.984 (2) Å
b = 16.588 (4) Å
c = 13.732 (2) Å
 β = 103.27 (2)°
V = 1991.8 (6) Å³
Z = 4
D_x = 1.232 Mg m⁻³
D_m not measured

Mo K α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 7.3–12.0°
 μ = 0.182 mm⁻¹
T = 293 (2) K
 Needle
 0.35 × 0.20 × 0.20 mm
 Colourless

Data collection

Rigaku AFC-6S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 3388 measured reflections
 3152 independent reflections
 1219 observed reflections
 $[I > 2\sigma(I)]$

*R*_{int} = 0.0587
 θ_{\max} = 24.99°
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 19$
 $l = -16 \rightarrow 15$
 3 standard reflections monitored every 150 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R(*F*) = 0.0659
 $wR(F^2) = 0.3392$
S = 1.078
 3129 reflections
 235 parameters
 H atoms riding with *U*(H) = 1.2*U*_{eq}(C)
 $w = 1/[\sigma^2(F_o^2) + (0.1506P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.289 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.253 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.0071 (2)	0.11537 (12)	0.83844 (15)	0.0722 (7)
O1	0.5435 (6)	-0.1254 (4)	0.9104 (4)	0.103 (2)
O2	-0.0652 (5)	0.0744 (3)	0.9061 (4)	0.088 (2)
O3	-0.0706 (5)	0.1248 (3)	0.7360 (4)	0.095 (2)
N1	0.1655 (5)	0.0622 (3)	0.8404 (4)	0.066 (2)
C2	0.2116 (7)	-0.0041 (4)	0.9004 (5)	0.060 (2)
C3	0.3488 (6)	-0.0317 (4)	0.8876 (5)	0.063 (2)
C4	0.3945 (7)	0.0231 (4)	0.8181 (5)	0.059 (2)
C5	0.5259 (8)	0.0276 (5)	0.7797 (6)	0.077 (2)
C6	0.5327 (9)	0.0866 (6)	0.7123 (6)	0.094 (3)
C7	0.4121 (10)	0.1410 (5)	0.6782 (6)	0.093 (3)
C8	0.2850 (8)	0.1373 (5)	0.7179 (5)	0.078 (2)
C9	0.2780 (7)	0.0770 (4)	0.7874 (5)	0.064 (2)
C10	0.4234 (8)	-0.1061 (4)	0.9316 (5)	0.069 (2)
C11	0.3458 (8)	-0.1571 (5)	0.9945 (6)	0.084 (2)
C12	0.4302 (9)	-0.2304 (5)	1.0398 (6)	0.089 (2)
C13	0.3462 (10)	-0.2770 (5)	1.1059 (7)	0.101 (3)
C14	0.4346 (13)	-0.3473 (7)	1.1594 (10)	0.149 (4)
C15	0.3520 (13)	-0.3886 (8)	1.2279 (10)	0.173 (6)
C16	0.0742 (7)	0.2090 (4)	0.8845 (5)	0.062 (2)
C17	0.0553 (9)	0.2752 (5)	0.8218 (6)	0.083 (2)
C18	0.1144 (10)	0.3489 (5)	0.8573 (7)	0.095 (3)
C19	0.1883 (9)	0.3593 (5)	0.9569 (7)	0.084 (2)
C20	0.2033 (9)	0.2913 (6)	1.0183 (6)	0.084 (2)
C21	0.1464 (8)	0.2179 (5)	0.9833 (6)	0.075 (2)
C22	0.2508 (12)	0.4394 (6)	0.9931 (7)	0.124 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

S1—O2	1.422 (5)	C3—C4	1.445 (9)
S1—O3	1.428 (5)	C3—C10	1.466 (9)
S1—N1	1.669 (5)	C4—C9	1.368 (8)
S1—C16	1.733 (7)	C4—C5	1.401 (9)
O1—C10	1.223 (7)	C5—C6	1.358 (11)
N1—C2	1.379 (8)	C6—C7	1.405 (11)
N1—C9	1.396 (8)	C7—C8	1.376 (10)
C2—C3	1.364 (8)	C8—C9	1.393 (9)
C2—N1—C9	107.3 (5)	C6—C5—C4	117.9 (7)
C2—N1—S1	124.7 (4)	C5—C6—C7	122.6 (7)
C9—N1—S1	128.0 (5)	C8—C7—C6	119.0 (8)
C3—C2—N1	110.4 (6)	C7—C8—C9	118.4 (7)
C2—C3—C4	106.0 (6)	C4—C9—C8	121.9 (6)
C9—C4—C5	120.0 (7)	C4—C9—N1	108.6 (6)
C9—C4—C3	107.6 (5)	C8—C9—N1	129.4 (6)
C5—C4—C3	132.4 (7)		

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*. Literature survey: *CSSR* (1984).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3,4,6,7,9,10-Hexahydro-3,3,6,6-tetramethyl-1,8(2H,5H)-dioxo-10-phenyl-9-acridinyl-methyl Acetate

K. GUNASEKARAN,^a D. VELMURUGAN,^{a*} P. MURUGAN,^b V. T. RAMAKRISHNAN,^b K. PANNEERSELVAM^c AND M. SORIANO-GARCÍA^c

^aDepartment of Crystallography and Biophysics,† University of Madras, Madras 600 025, India, ^bDepartment of Organic Chemistry, School of Chemistry, University of Madras, Madras 600 025, India, and ^cInstituto de Química, UNAM Circuito Exterior ed Universitaria, México DF 04510, México

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Abstract

The conformation of the title compound, $\text{C}_{26}\text{H}_{31}\text{NO}_4$, is folded. The substituents are in a *cis* orientation, even though they are bulky, which helps stacking interactions.

Comment

Acridine compounds are well known DNA intercalating agents (Neidle, 1979) and are involved in mutagenesis (Brenner, Barnett, Crick & Orgel, 1961; Orgel, 1965). In acridinediones, the electron delocalization along a stretch of nine non-H atoms results in fluorescence and laser activity (Selladurai, Subramanian & Ramakrishnan, 1990). The effectiveness of lasing can be controlled by the substituents at the N atom and at the C atom opposite the N atom of the acridine chromophore. With this in mind, the structure of 9-acetoxymethyl-

† DCB contribution No. 872.