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Azoles. 19.* Structure of 4-Nitro-7-phenylsulfonylmethylindazole

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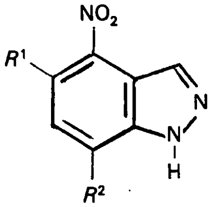
Abstract. $C_{14}H_{11}N_3O_4S$, $M_r = 317{\cdot}17$, monoclinic, $P2_1/n$, $a = 7{\cdot}842\,(1)$, $b = 13{\cdot}292\,(4)$, $c = 13{\cdot}734\,(3)$ Å, $\beta = 95{\cdot}47\,(1)^\circ$, $V = 1425{\cdot}2\,(6)$ Å^3, $D_m = 1{\cdot}48\,(1)$, $D_x = 1{\cdot}48$ Mg m^{-3}, $Z = 4$, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo }K\alpha) = 0{\cdot}201$ mm^{-1}, $F(000) = 656$, room temperature, final $R = 0{\cdot}035$ for 1647 observed reflections. The indazole system is strictly planar. The nitro group makes with it a dihedral angle of 2·0 (1)°. The phenyl ring of the phenylsulfonylmethyl substituent is turned by 13·4 (1)° out of the plane of the indazole system.

Introduction. The compound examined in this work was obtained by the action of chloromethyl phenyl sulfone on 4-nitroindazole. This reaction proceeds according to the mechanism of the vicarious nucleophilic substitution of hydrogen (Makosza, Kinowski, Danikiewicz & Mudryk, 1986). In this reaction the substitution takes place in *ortho* and/or *para* position(s) to the nitro group. Hence the product obtained can assume two different structures, *i.e.* (2) or (2*a*). It was not possible to determine the exact position of the newly introduced phenylsulfonylmethyl group on the basis of the analysis of the ^{1}H NMR spectrum, since its doublets at $\delta = 8{\cdot}08$ and 7·30 (both with the coupling constant of $J = 8$ Hz) might be attributed to two different pairs of hydrogen atoms in *ortho* position, *i.e.* 5 and 6 [compound (2)] or 6 and 7 [compound (2*a*)]. Unsuccessful attempts to obtain an *N*-acetyl derivative of the compound analyzed suggested structure (2) (Dudzińska-Usarewicz, Wrzeciono, Frankiewicz, Linkowska, Köhler & Nuhn, 1987). These suppositions were supported by X-ray analysis.



	R^1	R^2
(2)	H	$C_6H_5SO_2CH_2$
(2a)	$C_6H_5SO_2CH_2$	H

Experimental. Yellow prismatic crystals recrystallized from methanol, D_m by flotation, crystal dimensions $0{\cdot}55 \times 0{\cdot}5 \times 0{\cdot}25$ mm, Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, cell parameters from least-squares treatment of setting angles of 15 reflections with $18^\circ \le 2\theta \le 27^\circ$, θ–2θ scan technique, $2\theta \le 48^\circ$, two standard reflections monitored every 100 reflections, no significant intensity variation, no absorption correction, profiles measured for 2646 reflections, 2155 unique reflections, $R_{\text{int}} = 0{\cdot}044$, range of hkl: $h\ -8\rightarrow 8$, $k\ 0\rightarrow 14$, $l\ 0\rightarrow 15$, profile analysis according to Lehmann & Larsen (1974), 1647 reflections with $I \ge 1{\cdot}96\sigma(I)$ considered observed and used in the refinement, structure solved by direct methods using *SHELX*76 (Sheldrick, 1976), refinement on F by full-matrix least-squares method, refined $N = 244$ parameters, anisotropic non-H atoms, H atoms generated from ΔF map and refined as isotropic, $w^{-1} = \sigma^2(F)$, empirical isotropic extinction parameter x used to correct F_c according to $F_c' = F_c(1 - xF/\sin\theta)$, x converged at 0·005 (1), final $R = 0{\cdot}035$ and $wR = 0{\cdot}033$, $S = 2{\cdot}613$, $(\Delta/\sigma)_{\max} = 0{\cdot}05$, max. and min. height in the final ΔF map: 0·15 and $-0{\cdot}20$ e Å^{-3}; computer programs: *SHELX*76 (Sheldrick, 1976) and

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* Part 18: Dudzinska-Usarewicz, Wrzeciono, Frankiewicz, Linkowska, Kohler & Nuhn (1987).

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Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å²)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N(1)	0·7742 (3)	0·1857 (2)	0·7177 (2)	0·0463 (9)
N(2)	0·8844 (3)	0·1126 (2)	0·6954 (2)	0·056 (1)
C(3)	0·9574 (4)	0·1461 (2)	0·6195 (2)	0·051 (1)
C(4)	0·9237 (3)	0·3158 (2)	0·5195 (2)	0·0370 (9)
C(5)	0·8368 (4)	0·4049 (2)	0·5163 (2)	0·043 (1)
C(6)	0·7191 (3)	0·4253 (2)	0·5838 (2)	0·040 (1)
C(7)	0·6864 (3)	0·3572 (2)	0·6555 (2)	0·0333 (9)
C(8)	0·7774 (3)	0·2662 (2)	0·6569 (2)	0·0341 (8)
C(9)	0·8976 (3)	0·2429 (2)	0·5906 (2)	0·0366 (9)
N(10)	1·0417 (3)	0·2951 (2)	0·4463 (2)	0·0465 (9)
O(11)	1·1155 (3)	0·2137 (2)	0·4499 (1)	0·0627 (8)
O(12)	1·0615 (3)	0·3592 (2)	0·3833 (1)	0·0626 (8)
C(13)	0·5551 (3)	0·3777 (2)	0·7255 (2)	0·038 (1)
S(14)	0·35269 (9)	0·33011 (5)	0·67585 (5)	0·0402 (2)
O(15)	0·3673 (2)	0·2228 (1)	0·6663 (1)	0·0534 (7)
O(16)	0·2998 (2)	0·3882 (1)	0·5900 (1)	0·0536 (7)
C(17)	0·2130 (3)	0·3566 (2)	0·7659 (2)	0·0392 (9)
C(18)	0·1541 (4)	0·4537 (2)	0·7768 (2)	0·058 (1)
C(19)	0·0417 (5)	0·4729 (3)	0·8460 (3)	0·071 (1)
C(20)	−0·0095 (4)	0·3958 (3)	0·9038 (2)	0·066 (1)
C(21)	0·0495 (4)	0·2999 (3)	0·8936 (2)	0·059 (1)
C(22)	0·1619 (4)	0·2793 (2)	0·8241 (2)	0·047 (1)

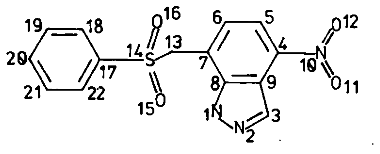

Fig. 1. Molecule with the numbering of atoms.

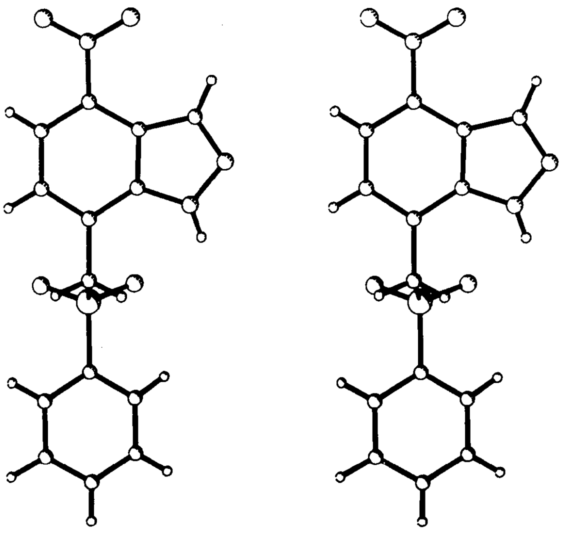

Fig. 2. Stereodrawing of the molecule.

local programs (Jaskólski, 1982), molecular illustrations drawn using *PLUTO* (Motherwell & Clegg, 1978). Atomic scattering factors from Sheldrick's programs.

Table 2. *Bond distances* (Å) *and angles* (°) *and their standard deviations*

N(1)—N(2)	1·355 (3)	N(10)—O(11)	1·226 (3)
N(1)—C(8)	1·358 (3)	N(10)—O(12)	1·235 (3)
N(2)—C(3)	1·314 (3)	C(13)—S(14)	1·783 (3)
C(3)—C(9)	1·412 (4)	S(14)—O(15)	1·437 (2)
C(4)—C(5)	1·364 (3)	S(14)—O(16)	1·436 (2)
C(4)—C(9)	1·405 (3)	S(14)—C(17)	1·764 (3)
C(4)—N(10)	1·456 (3)	C(17)—C(18)	1·384 (4)
C(5)—C(6)	1·396 (4)	C(17)—C(22)	1·385 (3)
C(6)—C(7)	1·379 (3)	C(18)—C(19)	1·380 (4)
C(7)—C(8)	1·404 (3)	C(19)—C(20)	1·379 (4)
C(7)—C(13)	1·499 (3)	C(20)—C(21)	1·368 (4)
C(8)—C(9)	1·406 (3)	C(21)—C(22)	1·386 (4)

C(8)—N(1)—N(2)	112·1 (2)	C(4)—N(10)—O(12)	118·9 (2)
N(1)—N(2)—C(3)	105·7 (2)	O(11)—N(10)—O(12)	123·1 (2)
N(2)—C(3)—C(9)	111·9 (3)	C(7)—C(13)—S(14)	109·3 (2)
C(5)—C(4)—C(9)	121·1 (2)	C(13)—S(14)—O(15)	108·1 (1)
C(5)—C(4) N(10)	119·4 (2)	C(13)—S(14)—O(16)	107·4 (1)
C(9)—C(4)—N(10)	119·5 (2)	O(15)—S(14)—O(16)	118·5 (1)
C(4)—C(5)—C(6)	120·4 (3)	C(13)—S(14)—C(17)	104·5 (1)
C(5)—C(6)—C(7)	121·8 (3)	O(15)—S(14)—C(17)	108·8 (1)
C(6)—C(7)—C(8)	116·5 (2)	O(16)—S(14)—C(17)	108·5 (1)
C(6)—C(7)—C(13)	121·6 (2)	S(14)—C(17)—C(18)	119·9 (2)
C(8)—C(7)—C(13)	121·9 (2)	S(14)—C(17)—C(22)	119·3 (2)
N(1)—C(8)—C(7)	130·3 (2)	C(18)—C(17)—C(22)	120·8 (3)
N(1)—C(8)—C(9)	106·1 (2)	C(17)—C(18)—C(19)	119·3 (3)
C(7)—C(8)—C(9)	123·5 (2)	C(18)—C(19)—C(20)	120·0 (3)
C(3)—C(9)—C(4)	139·2 (3)	C(19)—C(20)—C(21)	120·9 (3)
C(3)—C(9)—C(8)	104·1 (2)	C(20)—C(21)—C(22)	119·9 (3)
C(4)—C(9)—C(8)	116·7 (2)	C(17)—C(22)—C(21)	119·3 (3)
C(4)—N(10)—O(11)	117·9 (2)		

Discussion. The final atomic coordinates are given in Table 1.* Bond distances and angles are presented in Table 2. The numbering system is given in Fig. 1. A stereoview of the molecule is shown in Fig. 2.

The indazole part of the compound is planar. The maximum atomic deviation from the least-squares plane is 0·007 (3) Å. In the indazole system the geometry of the six-membered ring is deformed owing to the influence of a pyrazole ring fused to it along the C(8)—C(9) bond as well as to the presence of two substituents: the nitro and the phenylsulfonylmethyl groups. Thus, the bonds C(4)—C(5) [1·364 (3) Å] and C(6)—C(7) [1·379 (3) Å] are significantly shorter than in the unsubstituted benzene ring. The endocyclic angles on *ipso* α_{NO_2} and $\alpha_{C_6H_5SO_2CH_2}$ atoms take values of 121·1 (2) and 116·5 (2)°, respectively. In a compound not affected by the substituents mentioned above these assume values of 117·1 (2) and 117·4 (2)°, respectively (Leban, Stanovnik & Tišler, 1978). The nitro group is strictly coplanar with the C(4) atom and forms a dihedral angle of 2·0 (1)° with the plane of the indazole system. The C(4)—N(10) bond length [1·456 (3) Å] is slightly shorter than the C—N single bond (1·475 Å) (Sutton, 1958).

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* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates, torsion angles and weak hydrogen bonds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51451 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

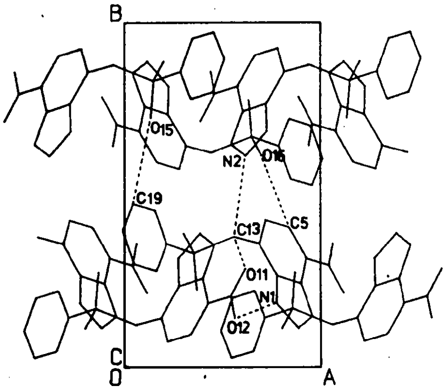

Fig. 3. Projection of the crystal structure along the *c* axis.

The phenyl ring of the $C_6H_5SO_2CH_2$— substituent is inclined to the indazole system at 13·4 (1)°. Its interatomic distances are in the range 1·368 (4)–1·386 (4) Å, with a mean value of 1·380 (4) Å, which is somewhat shorter than the ordinary aromatic bond length. The C(17)—S(14) bond distance of 1·764 (3) Å is comparable to the C(sp^2)—S single bond, *e.g.* 1·766 (2) Å (Sim, 1987), while that of S(14)—C(13), 1·783 (3) Å, is slightly shorter than the C(sp^3)—S (1·81 Å) single bond (*International Tables for X-ray Crystallography*, 1974). The bond distances S(14)—O(15) [1·437 (2) Å] and S(14)—O(16) [1·436 (2) Å] of the —SO_2— group are near to the expected value of 1·432 (3) Å for an S=O double bond (*International Tables for X-ray Crystallography*, 1974). A projection of the crystal structure is shown in Fig. 3. A hydrogen bond exists between the nitrogen and oxygen atoms with the following geometry: N(1)---O(12^i) 3·006 (3), H(11)---O(12^i) 2·18 (3) Å, N(1)—H(11)---O(12^i) 172 (2)°, (i) $-0·5 + x, 0·5 - y, 0·5 + z$. Moreover, weak intermolecular C—H---O and C—H---N hydrogen bonds were observed (Fig. 3).

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Azoles. 20.* Structure of a 2/1 Molecular Complex of 3,5-Dinitroindazole with Morpholine

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Abstract. $C_{18}H_{17}N_9O_9$, $M_r = 503·19$, monoclinic, $P2_1/n$, $a = 8·753$ (1), $b = 21·723$ (2), $c = 11·888$ (1) Å, $\beta = 99·39$ (1)°, $V = 2230·2$ (3) Å^3, $D_m = 1·50$ (1), $D_x = 1·50$ Mg m^{-3}, $Z = 4$, λ(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 0·954 mm^{-1}, $F(000) = 1040$, room temperature, final $R = 0·051$ for 2508 observed reflections. The asymmetric unit contains a molecular complex consisting of one morpholine and two 3,5-

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* Part 19: Gzella, Wrzeciono, Dudzińska-Usarewicz & Borowiak (1989).

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