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Acta Cryst. (1991). C**47**, 980–982

Azoles. 30.* Structure of the Molecular Complex of 3,5-Dinitroindazole with Thiomorpholine (1/1)

BY ANDRZEJ GZELLA AND URSZULA WRZECIONO†

Department of Organic Chemistry, Faculty of Pharmacy, K. Marcinkowski, Medical Academy, ul. Grunwaldzka 6, 60–780 Poznań, Poland

(*Received* 23 *January* 1990; *accepted* 20 *July* 1990)

Abstract. $(C_7H_4N_4O_4.C_4H_9NS)_2$, $M_r = 622{\cdot}63$, monoclinic, $C2/c$, $a = 20{\cdot}751\,(3)$, $b = 6{\cdot}782\,(1)$, $c = 20{\cdot}339\,(3)$ Å, $\beta = 102{\cdot}99\,(1)°$, $V = 2789{\cdot}3\,(7)$ Å^3, $Z = 4$, $D_m = 1{\cdot}48\,(1)$, $D_x = 1{\cdot}48$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 2{\cdot}175$ mm^{-1}, $F(000) = 1296$, room temperature, final $R = 0{\cdot}040$ for 1417 reflections. The molecular complex of 3,5-dinitroindazole and thiomorpholine lies on the 2 axis. The thiomorpholine molecule forms an $H_2N^+\!<$ ammonium cation as a result of the incorporation of a proton from the pyrrole N atom of the indazole moiety. The indazole system is approximately planar. The thiomorpholinium cation has a chair conformation; its least-squares plane makes a dihedral angle of 91·3 (1)° with the plane of the indazole system. Molecules in the complex are hydrogen bonded.

Introduction. In our preceding papers we described the X-ray structures of the molecular complexes of 3,5-dinitroindazole with morpholine [(I), Gzella, Wrzeciono & Borowiak, 1989], pyrrolidine [(II), Gzella & Wrzeciono, 1990] and piperazine [(III), Gzella & Wrzeciono, 1991]. This paper deals with the structure of the molecular complex of the same indazole derivative with thiomorpholine.

Experimental. The title compound, m.p. 475–476 K, was prepared by treating 3,5-dinitroindazole with thiomorpholine according to the method described by Wrzeciono & Linkowska (1980), yellow needle crystals recrystallized from propanol/water solution, D_m by flotation, crystal dimensions 0·4 × 0·3 × 0·2 mm, Syntex $P2_1$ diffractometer, graphite-monochromated Cu $K\alpha$ radiation, accurate lattice parameters from setting angles of 15 reflections with $11° \leq 2\theta \leq 33°$, θ–2θ scan technique, two standard reflections monitored every 100 reflections, no significant intensity variation, 1819 unique reflections, $R_{\mathrm{int}} = 0{\cdot}022$, range of hkl: h −21 to 21, k 0 to 8, l 0 to 21, profile analysis according to Lehmann & Larsen (1974), 1417 reflections with $I \geq 1{\cdot}96\sigma(I)$ considered observed and used in the refinement, structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refinement on F by full-matrix least-squares method, semi-empirical absorption corrections using *DIFABS* (Walker & Stuart, 1983),

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* Part 29: Gzella & Wrzeciono (1991).

† To whom correspondence should be addressed.

0108-2701/91/050980-03$03.00

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}
N(1)	0·3702 (1)	0·2272 (4)	0·2298 (1)	0·0409 (9)
N(2)	0·3967 (1)	0·2342 (4)	0·2970 (1)	0·0410 (9)
C(3)	0·3471 (1)	0·2318 (4)	0·3292 (1)	0·036 (1)
C(4)	0·2186 (1)	0·2211 (5)	0·2888 (2)	0·040 (1)
C(5)	0·1728 (1)	0·2167 (4)	0·2290 (2)	0·037 (1)
C(6)	0·1887 (2)	0·2156 (5)	0·1660 (2)	0·042 (1)
C(7)	0·2531 (2)	0·2174 (5)	0·1611 (2)	0·043 (1)
C(8)	0·3023 (1)	0·2219 (4)	0·2213 (1)	0·035 (1)
C(9)	0·2849 (1)	0·2241 (4)	0·2844 (1)	0·035 (1)
N(10)	0·3603 (1)	0·2455 (4)	0·4005 (1)	0·048 (1)
O(11)	0·4177 (1)	0·2591 (4)	0·4335 (1)	0·063 (1)
O(12)	0·3126 (1)	0·2466 (4)	0·4275 (1)	0·060 (1)
N(13)	0·1023 (1)	0·2128 (4)	0·2316 (2)	0·051 (1)
O(14)	0·0883 (1)	0·2118 (4)	0·2869 (1)	0·076 (1)
O(15)	0·0614 (1)	0·2059 (4)	0·1782 (1)	0·066 (1)
N(16)	0·4622 (1)	0·2464 (5)	0·1395 (1)	0·046 (1)
C(17)	0·4533 (2)	0·0478 (6)	0·1065 (2)	0·055 (1)
C(18)	0·3822 (2)	0·0070 (6)	0·0757 (2)	0·054 (1)
S(19)	0·34499 (5)	0·1834 (2)	0·01308 (4)	0·0658 (4)
C(20)	0·3694 (2)	0·4061 (6)	0·0601 (2)	0·060 (2)
C(21)	0·4419 (2)	0·4143 (6)	0·0918 (2)	0·058 (2)

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

N(1)—N(2)	1·354 (3)	C(8)—C(9)	1·408 (4)
N(1)—C(8)	1·380 (4)	N(10)—O(11)	1·233 (3)
N(2)—C(3)	1·339 (4)	N(10)—O(12)	1·236 (3)
C(3)—C(9)	1·403 (4)	N(13)—O(14)	1·222 (3)
C(3)—N(10)	1·417 (3)	N(13)—O(15)	1·221 (3)
C(4)—C(5)	1·366 (4)	N(16)—C(17)	1·497 (5)
C(4)—C(9)	1·399 (4)	N(16)—C(21)	1·494 (5)
C(5)—C(6)	1·393 (4)	C(17)—C(18)	1·493 (5)
C(5)—N(13)	1·476 (4)	C(18)—S(19)	1·792 (4)
C(6)—C(7)	1·363 (4)	S(19)—C(20)	1·798 (4)
C(7)—C(8)	1·408 (4)	C(20)—C(21)	1·500 (5)
N(2)—N(1)—C(8)	107·4 (2)	C(4)—C(9)—C(8)	121·0 (3)
N(1)—N(2)—C(3)	108·1 (2)	C(3)—N(10)—O(11)	120·2 (3)
N(2)—C(3)—C(9)	112·2 (2)	C(3)—N(10)—O(12)	117·7 (3)
N(2)—C(3)—N(10)	120·5 (3)	O(11)—N(10)—O(12)	122·1 (3)
C(9)—C(3)—N(10)	127·3 (3)	C(5)—N(13)—O(14)	118·4 (3)
C(5)—C(4)—C(9)	116·1 (3)	C(5)—N(13)—O(15)	117·8 (3)
C(4)—C(5)—C(6)	124·0 (3)	O(14)—N(13)—O(15)	123·8 (3)
C(4)—C(5)—N(13)	117·7 (3)	C(17)—N(16)—C(21)	114·0 (3)
C(6)—C(5)—N(13)	118·3 (3)	N(16)—C(17)—C(18)	111·5 (3)
C(5)—C(6)—C(7)	120·4 (3)	C(17)—C(18)—S(19)	113·7 (3)
C(6)—C(7)—C(8)	117·9 (3)	C(18)—S(19)—C(20)	99·1 (2)
N(1)—C(8)—C(9)	110·4 (2)	S(19)—C(20)—C(21)	113·3 (3)
C(7)—C(8)—C(9)	120·6 (3)	N(16)—C(21)—C(20)	111·1 (3)
C(3)—C(9)—C(8)	101·9 (3)		

anisotropic non-H atoms, H atoms from ΔF map and refined with isotropic temperature parameters, 243 refined parameters, $w^{-1} = \sigma^2(F)$, empirical isotropic extinction parameter x used to correct F_c according to $F_c' = F_c(1 - 0{\cdot}0001xF_c^2/\sin\theta)$, x converged to 0·0043 (1), final $R = 0{\cdot}040$ and $wR = 0{\cdot}041$, $S = 3{\cdot}831$, $(\Delta/\sigma)_{max} = 0{\cdot}04$, max. and min. heights in the final ΔF map 0·25 and −0·35 e Å^{-3}; other computer programs: *SHELX76* (Sheldrick, 1976) and local programs (Jaskólski, 1982), molecular illustrations drawn using *PLUTO* (Motherwell & Clegg, 1978). Atomic scattering factors from *SHELX76*.

Discussion. Table 1 lists the final atomic coordinates and equivalent isotropic temperature factors.* The bond lengths and angles are presented in Table 2. The numbering system is given in Fig. 1. A stereoview of the molecular complex is given in Fig. 2. The molecular complex consists of two molecules of 3,5-dinitroindazole and two molecules of thiomorpholine and lies in a special position on the 2 axis. The molecules forming the complex are linked by hydrogen bonds, the geometries of which are: N(16)—H(161) 0·86 (3), N(16)···N(1^{i}) 2·936 (4), H(161)---N(1^{i}) 2·09 (3) Å, N(16)—H(161)---N(1^{i}) 168 (3)°, N(16)—H(162) 1·03 (4), N(16)···N(2) 2·924 (4), H(162)---N(2) 1·90 (4) Å, N(16)—H(162)---N(2) 169 (3)° [symmetry code: (i) $1-x$, y, $0{\cdot}5-z$].

As a result of the incorporation of one proton from the pyrrole N atom, N(1), the thiomorpholine forms an $N_2N^+\!<$ ammonium cation. The indazole system is approximately planar, the maximum deviation [C(6) atom] from its least-squares plane being

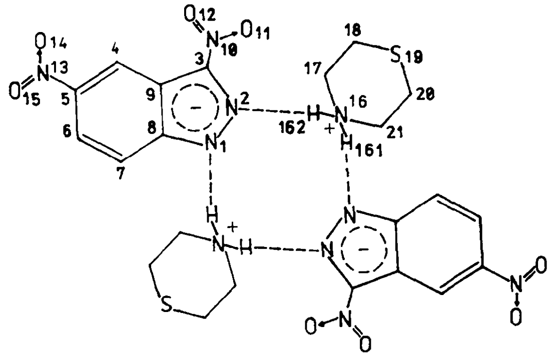

Fig. 1. Labelling system.

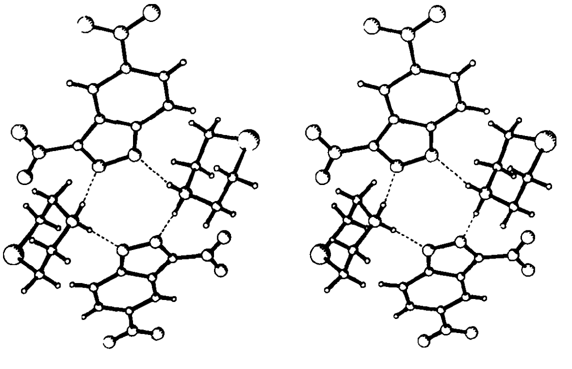

Fig. 2 Stereodrawing of the molecule.

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* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53419 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

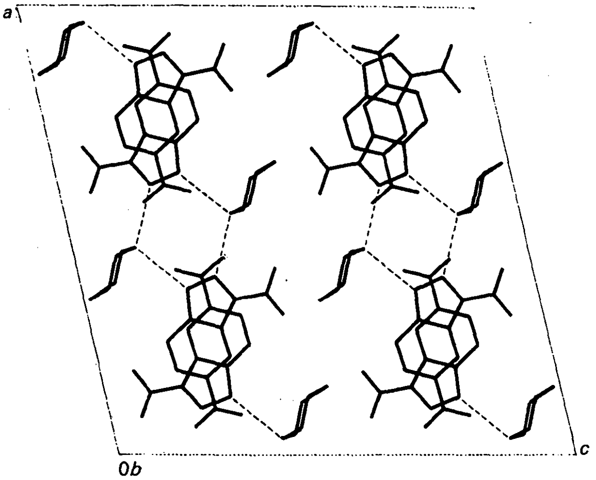

Fig. 3. Projection of the crystal structure along the *b* axis.

0·012 (3) Å. The thiomorpholinium cation has a chair conformation. The least-squares plane through it makes a dihedral angle of 91·3 (1)° with the plane of the indazole system.

The bond lengths and angles for the nitrobenzene part of 3,5-dinitroindazole (Table 2) are comparable with those found in (I), (II) and (III). The nitro group at C(5) lies in the plane of the indazole system. The plane of the —NO_2 group attached to the C(3) atom is inclined by 3·1 (1)° to the plane of the indazole system.

The negative charge of the N(1) atom of the pyrazole ring is presumably delocalized mainly through the bonds N(1)—N(2) [1·354 (3) Å] and N(2)—C(3) [1·339 (4) Å] for conjugation with the nitro group. The same bonds in (I) (molecule *B*), are 1·345 (3) and 1·321 (4) Å, respectively. Owing to the conjugation, the exocyclic bond C(3)—N(10) [1·417 (4) Å] is shorter than that [1·441 (4) Å] found in (I).

In the crystal lattice (Fig. 3), 3,5-dinitroindazole molecules are parallel and partly overlap, forming layers nearly perpendicular to **z**. However, there is no strong interaction between layers, the separation being *ca* 3·7 Å.

This work was supported by project RP.II.13.

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Acta Cryst. (1991). C**47**, 982–984

Structures of Trimethylsulfonium Salts. I. Refinement of the Structure of the Iodide $(CH_3)_3SI$

BY MICHEL JANNIN, RENÉ PUGET, CHRISTINE DE BRAUER AND RENÉ PERRET

Laboratoire de Physique du Solide, Associé au CNRS (*URA* 785), *Université de Bourgogne, BP* 138, 21004 *Dijon CEDEX, France*

(*Received* 30 *April* 1990; *accepted* 4 *July* 1990)

Abstract. Trimethylsulfonium iodide, $C_3H_9S^+.I^-$, M_r = 204·07, monoclinic, $P2_1/m$, a = 7·201 (2), b = 7·998 (2), c = 5·930 (2) Å, β = 94·87 (5)°, V = 340 (1) Å^3, Z = 2, D_x = 1·991, D_m = 1·98 (2) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 4·821 mm^{-1}, $F(000)$ = 192, T = 293 K, final R = 0·022, wR = 0·025 for 993 independent observed reflections. The structure consists of stacks of I^-

0108-2701/91/050982-03$03.00