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Hydrogen-bonded networks in 1*H*-indazoles: the case of 7-methyl-1*H*-indazole

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.039
wR factor = 0.115
Data-to-parameter ratio = 8.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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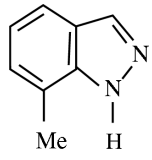
The secondary structure in the title compound, $C_8H_8N_2$, consists of infinite helical chains formed by molecules linked by N—H···N hydrogen bonds. Neighbouring chains are connected by C—H···π(azole) contacts.

Comment

The title compound, (I), has been studied in order to ascertain details of secondary structure, in the context of a project aimed at determining the influence of substituents on the different N—H···H hydrogen-bonding arrangements of azoles (Foces-Foces *et al.*, 2000). While 1*H*-unsubstituted pyrazole derivatives are well known nitrogen-containing heterocyclic compounds, structural studies of 1*H*-unsubstituted indazole derivatives are less common [Cambridge Structural Database (CSD), November 2003 release; Allen, 2002]. The structure of 5-phenylindazole (TELXUD; Hager *et al.*, 1996) has been reported previously, and its hydrogen-bonded network was compared with those already published. A search of the CSD reveals that the number of 1*H*-unsubstituted pyrazole structures has increased more rapidly than that of 1*H*-unsubstituted indazoles, *viz.* 66 *versus* nine organic compounds (hydrates, salts, inclusion complexes and compounds where at least one C substituent is a good hydrogen-bond donor are excluded). The number of hydrogen-bond motifs observed in 1*H*-pyrazoles, *i.e.* catemer, dimers, trimer, tetramers and, as shown recently, hexamers (HUMLUW; Haghiri *et al.*, 2002), contrasts with that observed in 1*H*-indazoles, where only catemers, trimers and, recently, dimers have been observed [FULKUS (Ooms *et al.*, 2000), FULKUS01 (Sopkova-de Oliveira Santos *et al.*, 2000) and TIJJUR (Gzella & Wrzeciono, 2001)]. This fact prompted us to determine the structure of the title compound, the molecular structure of which is shown in Fig. 1.



(I)

The molecules exist in the 1*H*-tautomeric form, (I), as in the previously reported analogues and in agreement with the theoretical results performed on this type of compound (Catalan *et al.*, 1996). The main differences in the molecular structures of the indazole (INDAZL), and the 7-nitro (FULKUS, FULKUS01) and 7-methoxy derivatives (IHESIX) are located at the endocyclic bond angle at atom

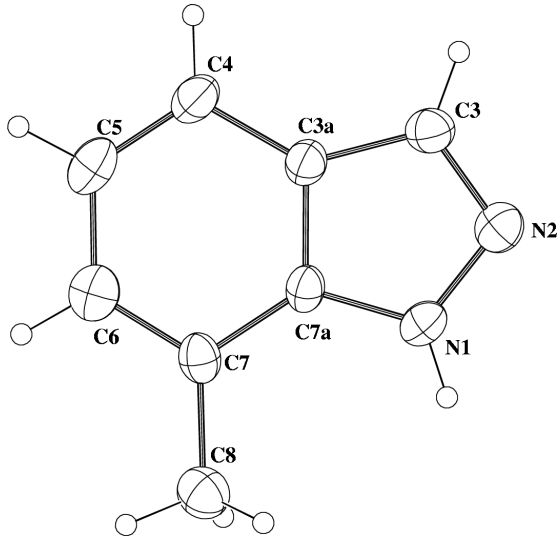


Figure 1
Molecular structure of (I), with 30% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

C7, which reflects the electronic withdrawing or donating character of the substituents, widening [NO_2: 119.4 (1)/ 119.5 (1)° in FULKUS/FULKUS01; OMe: mean 116.7 (4)° in IHESIX] and narrowing, respectively [Me in (I): 115.0 (3)°].

In the crystal structure, molecules form helical chains along **c**, created by N—H···N bonds (Figs. 2 and 3). Each catemer is formed by molecules related by twofold screw axes [H1···N2^{i} 2.12 Å, N1···N2^{i} 2.931 (3) Å and N1—H1···N2^{i} 156°; symmetry code: (i) $\frac{1}{2}-x$, $1-y$, $z-\frac{1}{2}$], the same as in the parent indazole and in the 5-phenyl derivative (TELXUD), whereas the nitro derivative forms dimers and the methoxy derivative trimers. Weak C—H···π(azole) interactions connect neighbouring chains [C6···Cg^{ii} 3.993 (3) Å, H6···Cg^{ii} 3.19 Å and C6—H6···Cg^{ii} 146°; symmetry code: (ii) $1-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$; *Cg* is the centroid of the azole ring].

The nine indazole derivatives in the CSD are distributed as follows: the parent compound (INDAZL), two compounds with substituent only at C3 (phenyl, two polymorphic forms UHENUQ/UHENUQ01, and methylcarboxy, SUHVUM), none at C4 or C6, one at C5 (phenyl, TELXUD), two at C7 (nitro, FULKUS/FULKUS01, and methoxy, IHESIX) and the remaining four with substituents at two or more C atoms (5-nitro-3-thiomorpholino, TIJJUR, 3-phenyl-5-methyl, VILPEL, and 4-nitro-7-phenylsulfonylmethyl, VUXWAM). In all cases, except in VUXWAM, where N—H···O═N bonds are present, the secondary structure is due to N—H···N bonds, which form catemers (INDAZL and TELXUD), dimers (FULKUS and TIJJUR) and trimers (INHESIX, UHENUQ/UHENUQ01, VILPEL and SUHVUM). Although the number of structures is very small for an insight into the relationship between the substituents and the secondary structure, the substituent at C5 seems not to affect the type of secondary structure, as occurs in indazole (INDAZL) and in 5-phenylindazole (TELXUD), which form chains, or between the two polymorphic forms of 3-phenylindazole (UHENUQ and UHENUQ01) and 3-phenyl-5-methylindazole (VILPEL), which form trimers.

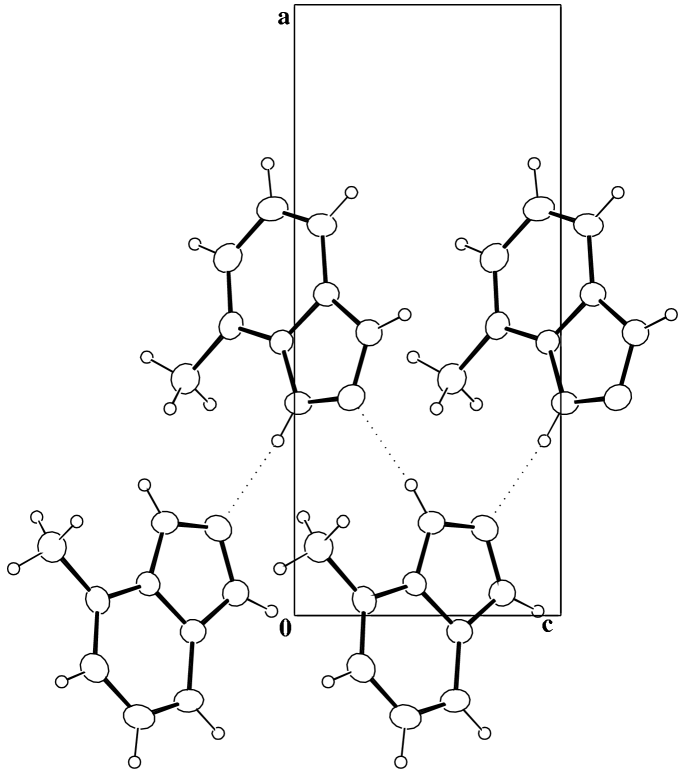


Figure 2
One-dimensional hydrogen-bonded framework in (I). Hydrogen bonds are shown as dotted lines.

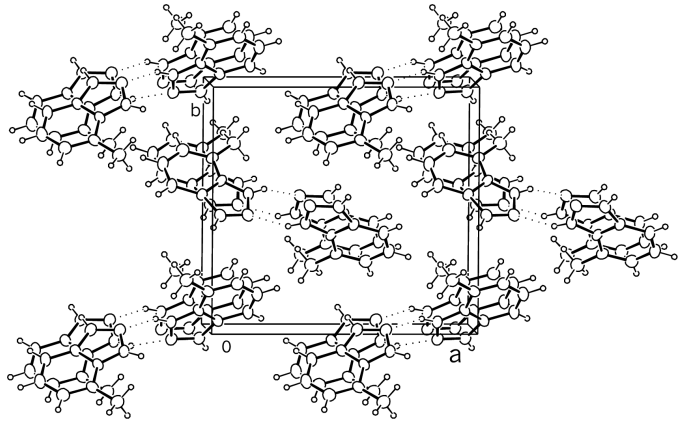


Figure 3
Packing diagram of (I), illustrating the disposition of the chains. Dotted lines indicate hydrogen bonds.

Experimental

The title compound was prepared according to the method of Fusco *et al.* (1987), and crystals suitable for X-ray analysis were grown at room temperature from ethanol.

Crystal data

$C_8H_8N_2$	D_x = 1.254 Mg m^{-3}
M_r = 132.16	Cu $K\alpha$ radiation
Orthorhombic, $P2_12_12_1$	Cell parameters from 47 reflections
a = 12.0013 (11) Å	θ = 2–45°
b = 11.1465 (11) Å	μ = 0.61 mm^{-1}
c = 5.2327 (4) Å	T = 295 (2) K
V = 699.99 (11) Å^3	Prism, colourless
Z = 4	0.50 × 0.20 × 0.13 mm

Data collection

Seifert XRD3000-S four-circle diffractometer	θ_{max} = 67.0°
$\omega/2\theta$ scans	$h = -14 \rightarrow 14$
Absorption correction: none	$k = -13 \rightarrow 13$
1504 measured reflections	$l = -6 \rightarrow 6$
759 independent reflections	2 standard reflections
692 reflections with $I > 2\sigma(I)$	frequency: 100 min
R_{int} = 0.047	intensity decay: 5.5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0704P)^2 + 0.0866P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.039	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.115	$\Delta\rho_{max}$ = 0.15 e Å^{-3}
S = 1.04	$\Delta\rho_{min}$ = −0.12 e Å^{-3}
759 reflections	Extinction correction: *SHELXL97*
92 parameters	Extinction coefficient: 0.070 (7)
H-atom parameters constrained	

All H atoms were located in difference Fourier maps and subsequently allowed to refine as riding on their respective C and N atoms, with N—H = 0.86 Å, C_{methyl}—H = 0.96 Å and other C—H = 0.93 Å. U_{iso}(H) was set to 1.2 (1.5 for methyl) times U_{eq} of the parent atom. Compound (I) is achiral but crystallizes in the non-centrosymmetric space group $P2_12_12_1$. Although it does not contain atoms heavier than N, all the Friedel pairs were collected using Cu radiation. Refinement of the Flack (1983) parameter led to a meaningless value of 0.1 (10) and, therefore, Friedel pairs were merged prior to the final refinement.

Data collection: *CRYSOM* (Seifert, 1996); cell refinement: *LSUCRE* (Appleman, 1984); data reduction: *Xtal3.6* (Hall *et al.*, 1999); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal3.6*; software used to prepare material for publication: *SHELXL97* and *WinGX* (Farrugia, 1999).

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References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Appleman, D. E. (1984). *LSUCRE*. US Geological Survey, Washington DC, USA.

Catalan, J., de Paz, J. L. G. & Elguero, J. (1996). *J. Chem. Soc. Perkin Trans.* 2, pp. 257–260.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Foces-Foces, C., Alkorta, I. & Elguero, J. (2000). *Acta Cryst.* B**56**, 1018–1028.

Fusco, R., Marchesini, Initial, A. & Sannicolo, F. (1987). *J. Heterocycl. Chem.* **24**, 773–778.

Gzella, A. & Wrzeciono, U. (2001). *Acta Cryst.* C**57**, 1189–1191.

Hager, O., Foces-Foces, C., Jagerovic, N., Elguero, J. & Trofimenko, S. (1996). *Acta Cryst.* C**52**, 2894–2896.

Haghiri, A., Lerner, H.-W. Wagner, M. & Bats, J. W. (2002). *Acta Cryst.* E**58**, o1378–o1380.

Hall, S. R., du Boulay, D. J. & Olthof-Hazekamp, R. (1999). Editors. *The Xtal3.6 System of Crystallographic Software. User's Manual.* The University of Western Australia, Australia.

Ooms, F., Norberg, B., Isin, E. M., Castagnoli, N.,Van der Schyf, C. J. & Wouters, J. (2000). *Acta Cryst.* C**56**, e474–e475.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Seifert (1996). *CRYSOM*. Version 2.8. Seifert & Cie., Ahrensburg, Germany.

Sopkova-de Oliveira Santos, J., Collot, V. & Rault, S. (2000). *Acta Cryst.* C**56**, 1503–1504.