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5-Phenylindazole

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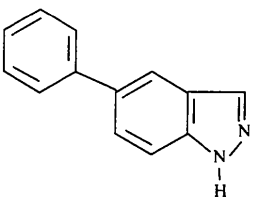
Abstract

The title compound, $C_{13}H_{10}N_2$, packs in chains along the *a* axis *via* N—H···N hydrogen bonds that are stronger and more linear than those observed in unsubstituted indazole. These chains are linked by C—H···N and C—H···phenyl contacts along **b**, giving rise to a wave-like structure.

Comment

We are interested in the proton tautomerism (prototropy) and the intermolecular hydrogen bonding of NH-pyrazoles (Llamas-Saiz, Foces-Foces & Elguero, 1994; Aguilar-Parrilla *et al.*, 1995; Elguero, Jagerovic *et al.*, 1995); the NH-indazoles are a subgroup of these compounds (Llamas-Saiz, Foces-Foces & Elguero, 1994). With regard to tautomerism, the literature suggests that only the 1*H*-tautomer is present in NH-indazoles, the 2*H*-tautomer being much less stable (Catalan, de Paz & Elguero, 1996). Two types of hydrogen-bonding network are possible for NH-indazoles, catemers and trimers. In the first group, indazole molecules (Escande & Lapasset, 1974) are linked by N—H···N hydrogen bonds while in 1*H*-indazole-3-carboxylic acid (Benetollo & Del Pra, 1993), the molecules are bonded through N—H···O bonds reinforced by O—H···N interactions. Trimers are formed *via* N—H···N bonds in 3-phenyl-5-methyl-1*H*-indazole (Dvorkin *et al.*, 1989) and *via* N—H···O/N three-centre bonds in 3-methoxycarbonyl-1*H*-indazole (Glaser, Mummert, Horan & Barnes, 1993).



(I)

The molecular structure of the title compound (I) (Fig. 1) compares well with that reported for indazole itself (Escande & Lapasset, 1974). There are no significant differences in terms of the achieved precision as tested by half-normal probability plots (Abrahams & Keve, 1971). There is also good agreement with the results of the *ab initio* calculation at MP2/6-31G** level for the 1*H*-indazole (Catalan, de Paz & Elguero, 1996), but some differences are worth noting. The free molecule presents a greater degree of charge delocalization in the five-membered ring. The N1—N2 and N2—C3 bonds appear to be longer and shorter, respectively, in the present compound. The differences in the C5—C6 and C6—C7 bonds, however, could be due to the phenyl ring attached to C5 which is twisted by 23.8 (4)° with respect to the indazole plane. The *ipso* angle at the phenyl ring as well as the C4—C5—C6 angle (Table 2) in the indazole moiety reflects the σ-withdrawing influence of the indazole and phenyl moieties (Domenicano & Vaciago, 1979).

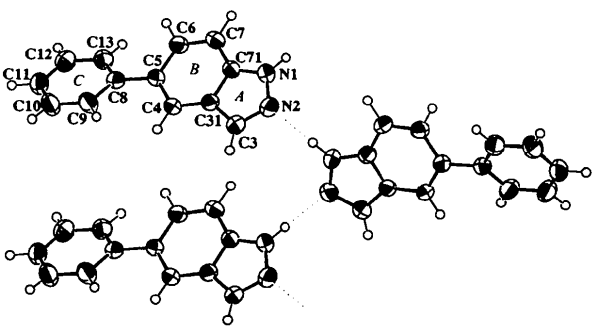


Fig. 1. The structure of 5-phenylindazole as projected along the *c* axis showing the atom labelling and the hydrogen-bonding system. Displacement ellipsoids are drawn at 50% probability level. The ring centroids are denoted by *A*, *B* and *C*. Dotted lines indicate hydrogen bonds.

A search of the Cambridge Structural Database (Allen *et al.*, 1991) shows that the C5—C8 distance and the C9—C8—C13 angle are similar to the values of 1.496 Å and 117.9° in the biphenyl compound (CSD refcode BIPHEN03; Charbonneau & Delugeard, 1976) although the benzene rings are inclined at an angle of 0.7°. These rings are twisted by up to 36.1° when the compound is co-crystallized with certain molecules (coordination complexes excluded), for instance perfluorobiphenyl (BPPFBP; Naae, 1979) but remain coplanar with 1,2,3,4-tetracyanobenzene (BUHSIG; Pasimeni, Guella, Carvaja, Clemente & Vicentini, 1983). This could be an indication that the lack of planarity may be due to packing forces.

The crystal packing, depicted in Fig. 2, is governed by the N1—H1···N2($\frac{1}{2}+x, \frac{1}{2}-y, 1-z$) hydrogen bonding (Table 3) which forms chains around a twofold screw axis parallel to the *a* axis; this bond is shorter and more linear than that reported for indazole [2.938 (10), 2.19 Å and 135°; Escande & Lapasset, 1974]. The chains are linked in the **b** direction by C—H···N contacts and *T*-type C—H···π-cloud (phenyl-ring) interactions (see Table 3). They result in a wave-like pattern in which alternating hydrophilic and hydrophobic zones can be observed.

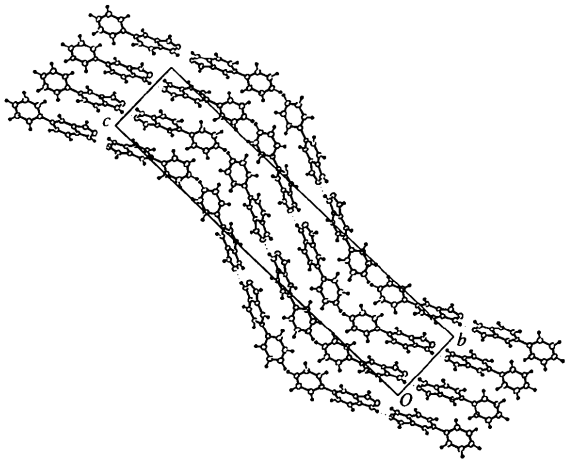


Fig. 2. View of the unit cell down the *a* axis showing the wave-like pattern and the alternating hydrophilic and the hydrophobic zones.

Experimental

4-Phenylcyclohexanone was formylated and then treated with hydrazine following the method used to make 3-phenylpyrazole by Trofimenko, Calabrese & Thompson (1987). The resulting 5-phenyltetrahydroindazole was purified by distillation [b.p. 473–478 K/2.5–2.8 Torr (1 Torr = 133.322 Pa)] and was obtained in 52% yield as a semi-crystalline syrup. This was heated with 5% Pd/C; hydrogen was evolved from 493 to 573 K. Upon completion, the residue was dissolved in boiling DMF, filtered through Celite and cooled, yielding 5-phenylindazole as shiny yellowish platelets in 46% yield (based on 4-phenylcyclohexanone). It was purified by sublimation followed by recrystallization from xylene; m.p. 504–505 K. Calculated for $C_{13}H_{10}N_2$: C 80.4, H 5.17, N 14.4; found C 80.3, H 5.27, N 14.3%. The crystals used were obtained by slow evaporation of a saturated solution in methanol. The ^{13}C NMR spectroscopy of this compound has been described by Elguero, Fruchier, Tjiou & Trofimenko (1995).

Crystal data

$C_{13}H_{10}N_2$
M_r = 194.23
Orthorhombic
Pbca
a = 5.9740 (4) Å
b = 8.2261 (7) Å
c = 40.685 (4) Å
V = 1999.4 (3) Å^3
Z = 8
D_x = 1.291 Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 58 reflections
θ = 2–45°
μ = 0.609 mm^{-1}
T = 293 K
Plate
0.40 × 0.40 × 0.10 mm
Colourless

Data collection

Seifert XRD3000-*S* diffractometer
$\omega/2\theta$ bisecting-geometry scans
Absorption correction: none
1931 measured reflections
1550 independent reflections
1122 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.001
θ_{max} = 64.89°
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 47$
2 standard reflections
frequency: 100 min
intensity decay: none

Refinement

Refinement on F
R = 0.038
wR = 0.044
S = 0.424
1122 reflections
177 parameters
Empirical weighting scheme
$(\Delta/\sigma)_{max}$ = 0.013
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 96 (10)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	U_{eq}
N1	0.5520 (4)	0.3310 (3)	0.52819 (5)	0.046 (1)
N2	0.3534 (4)	0.2507 (3)	0.52585 (5)	0.049 (1)
C3	0.2488 (5)	0.2743 (3)	0.55408 (6)	0.046 (1)
C31	0.3804 (4)	0.3697 (3)	0.57590 (6)	0.039 (1)
C4	0.3551 (4)	0.4281 (3)	0.60811 (6)	0.040 (1)
C5	0.5252 (4)	0.5195 (3)	0.62202 (5)	0.039 (1)
C6	0.7219 (4)	0.5500 (3)	0.60295 (6)	0.042 (1)
C7	0.7504 (5)	0.4951 (3)	0.57158 (6)	0.042 (1)
C71	0.5770 (4)	0.4026 (3)	0.55812 (6)	0.039 (1)
C8	0.5099 (4)	0.5805 (3)	0.65648 (6)	0.041 (1)
C9	0.3743 (5)	0.5046 (4)	0.67962 (7)	0.055 (2)
C10	0.3626 (6)	0.5599 (4)	0.71174 (7)	0.061 (2)
C11	0.4855 (5)	0.6919 (4)	0.72154 (6)	0.056 (2)
C12	0.6211 (6)	0.7685 (4)	0.69918 (7)	0.060 (2)
C13	0.6326 (5)	0.7142 (4)	0.66699 (7)	0.054 (2)

Table 2. *Selected geometric parameters (Å, °)*

N1—C71	1.361 (3)	C4—C5	1.385 (3)
N1—N2	1.362 (3)	C5—C6	1.431 (3)
N2—C3	1.322 (3)	C5—C8	1.492 (3)
C3—C31	1.422 (4)	C6—C7	1.365 (3)
C31—C4	1.404 (3)	C7—C71	1.397 (4)
C31—C71	1.405 (3)		
C71—N1—N2	111.6 (2)	C4—C5—C6	118.4 (2)
C3—N2—N1	106.2 (2)	C7—C6—C5	123.5 (2)
N2—C3—C31	111.3 (2)	C6—C7—C71	117.0 (2)
C4—C31—C71	120.3 (2)	N1—C71—C7	131.9 (2)
C4—C31—C3	135.4 (2)	N1—C71—C31	106.6 (2)
C71—C31—C3	104.3 (2)	C7—C71—C31	121.5 (2)
C5—C4—C31	119.2 (2)	C13—C8—C9	117.0 (2)
C4—C5—C8—C9	23.8 (4)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N2^{i}	0.89 (3)	2.05 (3)	2.920 (3)	164 (2)
C7—H7···N2^{ii}	1.03 (3)	2.78 (3)	3.670 (3)	145 (2)
C3—H3···Ring B^{iii}	0.98 (3)	2.68 (3)	3.460 (3)	136 (3)
C9—H9···Ring C^{iii}	0.99 (3)	2.89 (3)	3.770 (3)	149 (2)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, z$.

The structure was determined by direct methods. The H atoms were located on a difference Fourier map and refined freely with isotropic displacement parameters in the last cycles of refinement. An empirical weighting scheme was found to give no trends in $<w\Delta^2F>$ *versus* $<|F_o|>$ and $<\sin\theta/\lambda>$ using *PESOS* (Martinez-Ripoll & Cano, 1975). Structural details were extracted with the aid of *PARST* (Nardelli, 1983).

Data collection: Seifert XRD3000-*S* software. Cell refinement: *LSUCRE* (Appleman, 1983). Data reduction: *Xtal*3.2 *DIFDAT SORTREF ADDREF* (Hall, Flack & Stewart, 1994). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *Xtal*3.2. Software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Hydroxy-1,4-naphthoquinone

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Abstract

The title compound, $C_{10}H_6O_3$, crystallizes with two molecules per asymmetric unit. In both molecules, the naphthoquinone ring system is approximately planar, with the hydroxyl H atoms located in the plane. The crystal packing shows the molecules assembled in infinite linear chains by means of O—H···O hydrogen bonds between alternating independent molecules.

Comment

The crystal structure of the title compound, (I), was determined in order to study its packing in relation to the various substituted derivatives of this compound