although the anomalous dispersion terms for O, N and C are small. The absolute structure was not determined [Flack parameter −0.9 (12)] by our X-ray analysis, but can be inferred from the known absolute configuration of the L-leucine methyl ester derivative used in the synthesis. The H atoms attached to O and N were located from difference maps at an intermediate stage of refinement and were refined with isotropic displacement parameters. The N—H and two O—H distances refined to 0.84 (3), 0.88 (4) and 0.87 (3) Å, respectively. The H atoms attached to C were treated as riding atoms, with the C—H bond lengths in the range 0.93 to 0.98 Å.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC Software*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1997*a*) and *PLUTON* (Spek, 1997*b*). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *PRPCIF*97 (Ferguson, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1269). Services for accessing these data are described at the back of the journal.

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1-Phenyltetrazole

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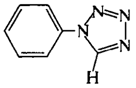
(*Received 9 March 1998; accepted 16 July 1998*)

Abstract

The tetrazole ring of the title compound, 1-phenyl-1*H*-1,2,3,4-tetrazole, $C_7H_6N_4$, should be an aromatic system. Slight conjugation effects are present between the phenyl and tetrazole rings. The two rings are not coplanar and have a dihedral angle of 11.8 (1)° between them.

Comment

As part of a study of the aromaticity of tetrazole rings, we are interested in the interaction between tetrazole and phenyl rings. The crystal data of the title compound, (I), was reported by Bryden (1969), but the crystal structure was not determined. We therefore determined the crystal structure of (I) using X-ray crystallographic methods.



(I)

Slight conjugation effects between the phenyl and tetrazole rings are present in (I). The N1—C2 bond length is 1.431 (2) Å, which is almost the same as the normal N—C_{phenyl} single-bond length. Moreover, the tetrazole and phenyl rings are not coplanar [dihedral angle 11.8 (1)°]. These facts indicate that there are slight resonance effects between the two rings.

Ab initio calculations also support the distorted conformation. At the MP2/6-31G* level, the most stable structure has a dihedral angle of 38.6° and is 4.12 kJ mol^{-1} more stable than the coplanar structure. Such a distorted conformation arises due to a steric interaction between the tetrazole ring 5-H atom (H1) and an *ortho*-H atom in the phenyl substituent (H7); the non-bonded distance between these two H atoms in the coplanar structure has been calculated to be 2.23 Å, which is sufficiently close considering the van der Waals radius of 1.20 Å for hydrogen.

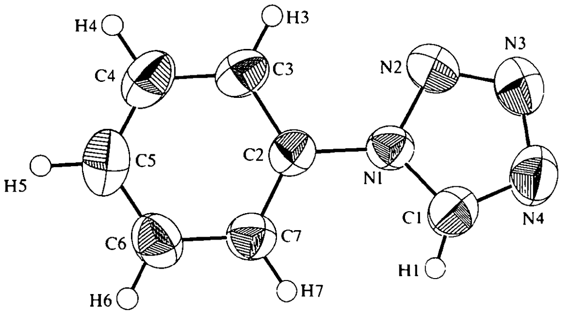


Fig. 1. View of the title molecule with the atomic numbering scheme and with non-H atoms represented by 50% probability ellipsoids.

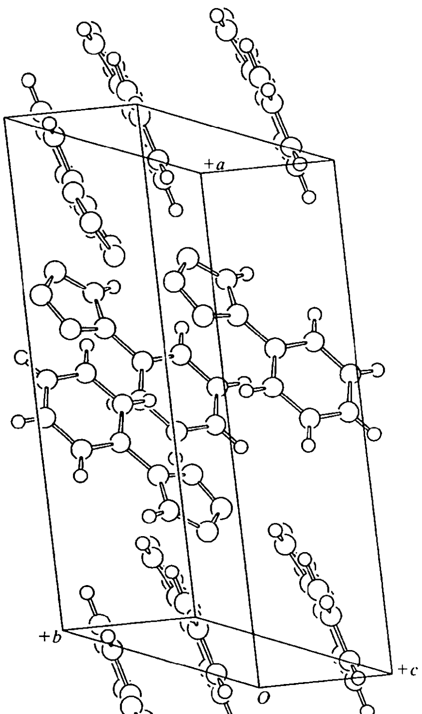


Fig. 2. Packing diagram of the title compound.

Experimental

The crystal of (I) used for analysis was obtained by recrystallization from acetone.

Crystal data

$C_7H_6N_4$
$M_r = 146.15$
Monoclinic
$P2_1/a$
$a = 15.146\,(6)$ Å
$b = 10.936\,(4)$ Å
$c = 4.328\,(1)$ Å
$\beta = 97.50\,(2)°$
$V = 710.7\,(4)$ Å^3
$Z = 4$
$D_x = 1.3659$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 17 reflections
$\theta = 8.37–12.27°$
$\mu = 0.092$ mm^{-1}
$T = 296$ K
Prism
$0.70 \times 0.30 \times 0.10$ mm
Colourless

Data collection

MacScience MXC18 diffractometer
ω scans with profile analysis
Absorption correction: none
1999 measured reflections
1403 independent reflections
1014 reflections with $F < 2\sigma(F)$

$R_{\rm int} = 0.027$
$\theta_{\rm max} = 27.5°$
$h = -19 \rightarrow 19$
$k = 0 \rightarrow 14$
$l = -5 \rightarrow 0$
3 standard reflections every 100 reflections intensity decay: 1.053%

Refinement

Refinement on F
$R = 0.053$
$wR = 0.041$
$S = 1.406$
1014 reflections
100 parameters
H atoms not refined
$w = \exp[5(\sin\theta)^2/\lambda^2]/[\sigma^2(F_o) + 0.0009|F_o|^2]$

$(\Delta/\sigma)_{\rm max} = 0.045$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

C1—N1	1.344 (2)	N1—N2	1.348 (2)
C1—N4	1.302 (2)	N2—N3	1.298 (2)
C2—N1	1.431 (2)	N4—N3	1.354 (2)
N1—C1—N4	109.6 (1)	C2—N1—N2	122.1 (1)
C3—C2—N1	118.0 (1)	N1—N2—N3	106.6 (1)
C7—C2—N1	119.8 (1)	C1—N4—N3	105.8 (1)
C1—N1—C2	130.6 (1)	N2—N3—N4	110.7 (1)
C1—N1—N2	107.3 (1)		
N4—C1—N1—C2	−179.1 (2)	C7—C2—N1—N2	169.1 (2)
N4—C1—N1—N2	−0.8 (1)	N1—C2—C7—C6	−179.6 (2)
N1—C1—N4—N3	0.7 (1)	C1—N1—N2—N3	0.5 (1)
C3—C2—N1—C1	166.8 (2)	C2—N1—N2—N3	179.0 (2)
N1—C2—C3—C4	179.6 (2)	N1—N2—N3—N4	0.0 (1)
C3—C2—N1—N2	−11.2 (1)	C1—N4—N3—N2	−0.4 (1)
C7—C2—N1—C1	−12.8 (1)		

All *ab initio* calculations were performed with the *GAUSSIAN*94 program package (Frisch *et al.*, 1995). The twisted structure was obtained by full optimization and the coplanar structure was obtained by partial optimization where the dihedral angle was fixed to be 0°. The structure was solved by direct methods and difference Fourier synthesis, and was refined by full-matrix least-squares methods with anisotropic displacement parameters for all non-H atoms. H atoms were located using a difference electron-density map and were included in the structure-factor calculations but were not refined.

Data collection: MacScience MXC18K software. Cell refinement: *CRYSTAN-GM* (Mackay *et al.*, 1995). Data reduction: *maXus* (Mackay *et al.*, 1998). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *maXus*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CRYSTAN-GM* and *maXus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1063). Services for accessing these data are described at the back of the journal.

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β Metal-free phthalocyanine

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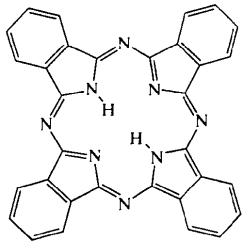
Abstract

The molecule of the title compound, $C_{32}H_{18}N_8$, is slightly distorted at the corners. Two of the phenyl rings are located below the molecular plane while the other two are above the plane. This leads to a molecular symmetry of C_i as opposed to D_{2h}, assumed for the free molecule. The crystal data are basically in good agreement with the β phase reported by Robertson [*J. Chem. Soc.* (1936), pp. 1195–1209], whereas the geometrical parameters are slightly different.

Comment

Metal-free phthalocyanine (MfPc) is a commercial blue pigment which is widely used in the paint and automobile industries. Besides its use as a pigment, MfPc has also attracted attention as a photoconductor for laser printers based on GaAsAl laser diodes (Loutfy *et al.*, 1988). Several crystal modifications such as α, β, *X etc.* are known to exist from X-ray powder diffraction, among which only the β phase has been fully analyzed on the basis of single crystals (Robertson, 1936).



MfPc

In the course of our studies on the mechanism of the near-IR absorption of titanylphthalocyanine (TiOPc), used practically for laser printers, we found that the molecules are heavily deformed upon crystallization ($C_{4v}\rightarrow C_1$) (Mizuguchi *et al.*, 1995). It was also pointed out that the molecular distortion (reduction in symmetry) has a profound influence on the optical absorption, because it removes the doubly-degenerate excited state to give two optical absorption bands in the visible region. Our attention is therefore focused on the electronic characterization of representative phthalocyanines from the aspect of molecular distortion. We have recently recognized that the structure of MfPc determined by Robertson (1936) was perfect for an experimental set-up at that time, but not precise enough for the examination of molecular distortion. For this reason, the present structure determination was undertaken.

The crystal structure is basically in good agreement with the β phase reported by Robertson (1936). The molecule is slightly distorted at the four corners. Two of the phenyl rings are located below the molecular plane while the other two are raised above the plane by 1.9 (2) (C2, C3, C4, C5, C6, C7) and 2.3 (2)° (C10, C11, C12, C13, C14, C15), respectively. This leads to a molecular symmetry of C_i as opposed to D_{2h}, assumed for the free molecule. This small molecular deformation

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