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Bis(5-phenyltetrazol-2-yl)methane

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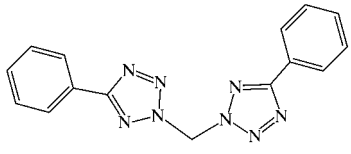
In the title compound, alternatively named 5,5′-diphenyl-2,2′-methyleneditetrazole, $C_{15}H_{12}N_8$, the dihedral angles between the tetrazole and benzene rings in the two 5-phenyltetrazole fragments are 2.45 (6) and 10.01 (9)°. There is weak intermolecular C—H···N hydrogen bonding involving the H atoms of the methylene groups, which is responsible for the formation of two-membered aggregates. C—H···π interactions in the crystal structure are discussed.

Comment

In recent years, binuclear tetrazoles have been of great interest, owing to their potential effectiveness as chelating agents and also due to their potential use as starting materials for the synthesis of some organometallic structures with important physical properties (Saalfrank *et al.*, 1995, 1996; Lyakhov *et al.*, 2001, and references therein). Of special interest are tetrazole compounds with activated methylene groups, which are very promising in organic fine synthesis (Dashkovskaya *et al.*, 1990; Brekhov *et al.*, 1992). In the light of this interest, we have prepared the title compound, (I), and present its crystal structure here.



(I)

The molecule of (I) (Fig. 1) contains two 5-phenyltetrazole fragments, denoted *A* and *B*. The geometrical parameters of the tetrazole rings of the 5-phenyltetrazole fragments in (I) are very similar (Table 1); corresponding bond distances and angles of the rings fall within the 3σ range. The tetrazole ring geometry is typical for 2,5-disubstituted tetrazoles (Cambridge Structural Database, Version 5.22 of October 2001; Allen & Kennard, 1993), with the following main features. The tetrazole rings are planar, to within 0.0016 (7) and 0.0027 (7) Å for fragments *A* and *B*, respectively. The N3—N4 bond is the shortest in the ring, while the N4—C5 bond is essentially longer than N1—C5. All the bond distances of the tetrazole rings, with the exception of N4—C5, lie within the narrow ranges 1.3127 (16)–1.3333 (14) (fragment *A*) and 1.3131 (16)–1.3287 (13) Å (fragment *B*). This is indicative of the greater aromatic character of the ring in 2,5-substituted tetrazoles in comparison with 1-mono-, 5-mono- and 1,5-disubstituted tetrazoles.

The benzene rings in (I) are planar to within 0.0038 (11) and 0.0030 (9) Å for 5-phenyltetrazole fragments *A* and *B*, respectively. The bond distances and angles are consistent with those observed previously for the ring (Allen & Kennard, 1993).

The benzene and tetrazole rings in (I) were found to be non-coplanar in the 5-phenyltetrazole fragments, the dihedral angles between the rings being 2.45 (6) and 10.01 (9)° for fragments *A* and *B*, respectively.

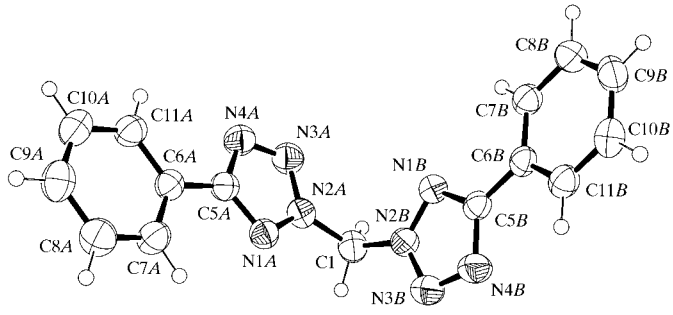


Figure 1
A view of the molecular structure of (I), showing the atom-labelling scheme for the two 5-phenyltetrazole fragments. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

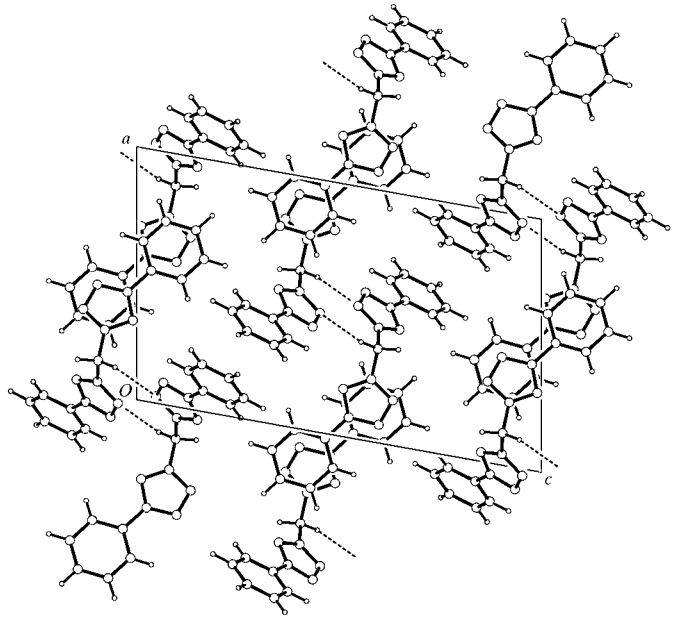


Figure 2
The crystal structure of (I), viewed along the *b* axis. Dashed lines indicate C—H···N hydrogen bonding.

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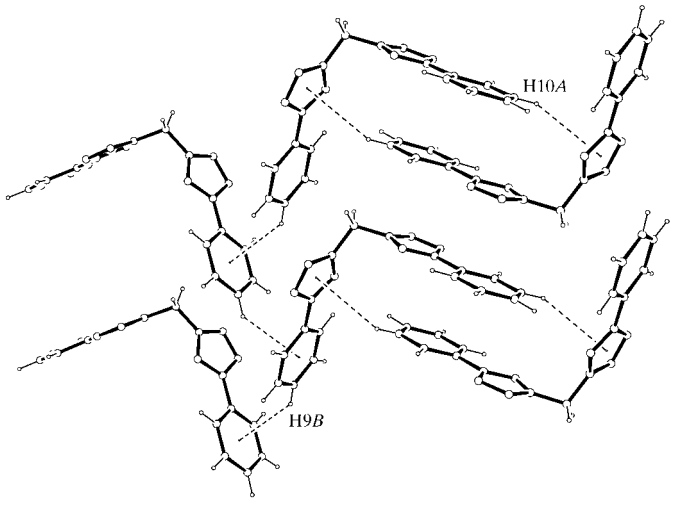

Figure 3
The C—H···π interactions in the structure of (I), viewed along the direction close to [001].

With regard to the packing structure, the following features may be noted (Spek, 1999). There are no classical hydrogen bonds in the structure of (I), but weak intermolecular C1—H1*B*···N3*B*^{i} hydrogen bonds are observed [Table 2; symmetry code: (i) $-x, 1-y, -z$]. These bonds are responsible for the formation of two-membered aggregates (Fig. 2).

Two types of intermolecular C—H···π interactions are detected in the structure of (I) (Fig. 3 and Table 2). The first type corresponds to the interactions between atom H10*A* of one molecule and the *B* tetrazole π-ring of another molecule at $(1-x, -y, -z)$. These interactions are characterized by the angle C10*A*—H10*A*···*Cg*···Tz of 141.6 (12)° and the distance H10*A*···*Cg*Tz of 3.116 (16) Å (*Cg*Tz denotes the centroid of the tetrazole ring). These interactions form two-membered entities, as shown in Fig. 3.

Atom H9*B* of one molecule and the *B* benzene π-ring of another molecule at $(-\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{2}-z)$ are involved in C—H···π interactions of the second type. These interactions are characterized by the angle C9*B*—H9*B*···*Cg*Bz of 140.1 (13)° and the distance H9*B*···*Cg*Bz of 2.877 (16) Å (*Cg*Bz denotes the centroid of the benzene ring). These interactions form chains extended along the *b* axis and link together the two-membered entities mentioned above, forming layers which are connected by C—H···N hydrogen bonds (Figs. 2 and 3).

As can be seen from Fig. 3, the crystal structure of (I) is also a subject for investigations of $\pi_{Bz}\cdots\pi_{Tz}$ stacking interactions.

Experimental

To prepare the title compound, a solution of 5-phenyltetrazole (0.06 mol), diiodomethane (0.03 mol) and triethylamine (0.06 mol) in dimethylformamide (50 ml) was agitated at 373 K for 20 h. The solution was cooled to room temperature and diluted with water (1 litre). The oil which formed was left to crystallize for several hours. The precipitate was filtered, washed with water and vacuum dried (yield 59%). Crystals of (I) suitable for single-crystal X-ray analysis were grown by slow evaporation from an ethyl acetate solution (m.p. 463–465 K, decomposition, uncorrected). Spectroscopic analysis: ^{1}H NMR (100 MHz, DMSO-d_6, δ, p.p.m.): 7.50–7.68 (*m*, 6H, C_6H_5), 7.88 (*s*, 2H, CH_2), 8.0–8.21 (*m*, 4H, C_6H_5).

Crystal data

$C_{15}H_{12}N_8$
M_r = 304.33
Monoclinic, $P2_1/n$
a = 11.053 (2) Å
b = 7.409 (2) Å
c = 17.956 (4) Å
β = 100.16 (2)°
V = 1447.4 (6) Å^3
Z = 4
D_x = 1.397 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 17.5–21.8°
μ = 0.09 mm^{-1}
T = 293 (2) K
Prism, colourless
0.50 × 0.45 × 0.40 mm

Data collection

Nicolet *R*3*m* four-circle diffractometer
$\omega/2\theta$ scans
4606 measured reflections
4258 independent reflections
3025 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 30.1°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = -25 \rightarrow 24$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.126
S = 1.04
4258 reflections
256 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2 + 0.0755P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N2*A*	1.4470 (16)	C5*A*—C6*A*	1.4645 (17)
C1—N2*B*	1.4535 (16)	N1*B*—C5*B*	1.3242 (15)
N1*A*—C5*A*	1.3271 (15)	N1*B*—N2*B*	1.3287 (13)
N1*A*—N2*A*	1.3333 (14)	N2*B*—N3*B*	1.3200 (15)
N2*A*—N3*A*	1.3223 (14)	N3*B*—N4*B*	1.3131 (16)
N3*A*—N4*A*	1.3127 (16)	N4*B*—C5*B*	1.3564 (15)
N4*A*—C5*A*	1.3579 (15)	C5*B*—C6*B*	1.4677 (16)
N2*A*—C1—N2*B*	110.18 (10)	C5*B*—N1*B*—N2*B*	101.67 (9)
C5*A*—N1*A*—N2*A*	101.65 (10)	N3*B*—N2*B*—N1*B*	114.19 (10)
N3*A*—N2*A*—N1*A*	114.11 (10)	N4*B*—N3*B*—N2*B*	105.72 (10)
N4*A*—N3*A*—N2*A*	105.71 (10)	N3*B*—N4*B*—C5*B*	106.53 (10)
N3*A*—N4*A*—C5*A*	106.75 (10)	N1*B*—C5*B*—N4*B*	111.88 (11)
N1*A*—C5*A*—N4*A*	111.77 (10)		

Table 2
Hydrogen-bonding geometry (Å, °).

*Cg*Tz is the centroid of the tetrazole ring and *Cg*Bz is the centroid of the benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···N3*B*^{i}	1.003 (15)	2.548 (15)	3.5324 (18)	166.9 (12)
C10*A*—H10*A*···*Cg*Tz^{ii}	0.961 (16)	3.116 (16)	3.9153 (18)	141.6 (12)
C9*B*—H9*B*···*Cg*Bz^{iii}	0.946 (18)	2.877 (16)	3.6548 (18)	140.1 (13)

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

H-atom positions were found in a difference Fourier map and all associated parameters were refined freely [C—H = 0.95 (2)–1.01 (2) Å].

Data collection: *R*3*m Software* (Nicolet, 1980); cell refinement: *R*3*m Software*; data reduction: *R*3*m Software*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1109). Services for accessing these data are described at the back of the journal.

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