Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Diethylammonium 5-phenyltetrazolate

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.005 Å
R factor = 0.049
wR factor = 0.107
Data-to-parameter ratio = 6.3

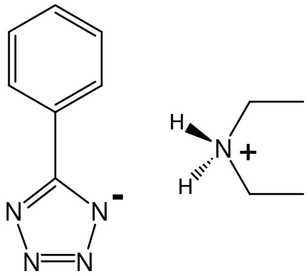
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 10 July 2002
Accepted 23 July 2002
Online 31 July 2002

The title compound, $[(C_2H_5)_2NH_2]^+[C_6H_5CN_4]^-$, crystallizes as discrete ions, linked by two types of hydrogen bonds into one-dimensional chains. The dihedral angle between the aromatic rings in the anion is 22.20 (12)°. The negatively charged 5-phenyltetrazolate moiety often serves as a ligand in main and transition metal complexes but, to our knowledge, this is the first example where it is not coordinated to a metal.

Comment

During our studies of early transition metal complexes with all-nitrogen coordination spheres, compound (I) was isolated as a side product and subsequently characterized crystallographically. The importance of this compound is twofold. Firstly, there is a limited number of structural studies of 5-substituted 1*H*-tetrazoles. Secondly, substituted tetrazoles are viable ligands observed in main and transition metal complexes in which they exhibit a variety of coordination modes. Compound (I) serves as a reference point for comparison of bond distances and angles within the tetrazolate ring in metal-coordinated and uncoordinated tetrazolate ligands. To our knowledge, this is the first example where a negatively charged phenyltetrazolate moiety is reported in the absence of a metal center. The four most relevant structures are 1*H*-5-phenyltetrazole, (II) (Krygowski & Cyranski, 1996), 1,2-bis(tetrazol-5-yl)benzene tetrahydrate, (III) (Bethel *et al.*, 1999), 5-(4-hydroxyphenyl)tetrazole–water (2/3), (IV) (Gallardo *et al.*, 1997), and 5-(2,4-dihydroxyphenyl)tetrazole sesquihydrate, (V) (Gallardo *et al.*, 1995).



(I)

The ionic compound (I) consists of discrete anions of 5-phenyltetrazolate (5-PhTz$^-$) and diethylammonium cations. The ions are connected by two types of hydrogen bonds (Table 2), forming infinite linear chains in the *c* direction.

The 5-PhTz$^-$ moiety contains two planar aromatic rings, with a 22.20 (12)° dihedral angle between them. The non-coplanarity of the two rings is caused by the intermolecular packing interactions in the lattice; molecular-modeling calculations, as expected, show that the planar geometry is the most

DOI: 10.1107/S1600536802013351

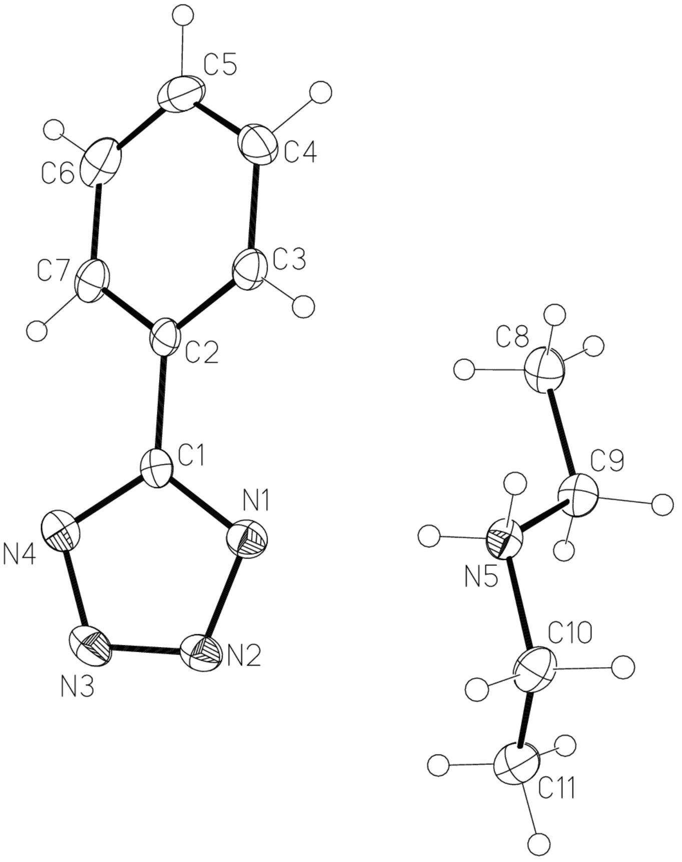


Figure 1
The molecular structure of (I), shown with 50% displacement probability ellipsoids.

energetically favorable. The corresponding angles were found to be 33.13 and 35.90° in (III), and 14.8 (1)° in (IV), while (II) and (V) contained planar conjugated π-systems delocalized over both rings.

The N2—N3 bond [1.307 (3) Å] is significantly shorter than other interatomic distances within the heterocycle despite the aromatic nature of the ring. The N2—N3 distances in (II), (III), (IV) and (V) are 1.282 (4), average 1.293 (3), 1.286 (2) and 1.286 (3) Å, respectively. The N2—N3 bond in (I) is longer than the latter four bonds and the difference is statistically significant. Nonetheless, the N2—N3 bond in (I) undoubtedly possesses double-bond character. The other bond distances and angles are in good agreement among the five structures. Thus, deprotonation of 5-phenyltertazole leads to a noticeable elongation of bond distances within the heterocycle. *Ab initio* calculations are in excellent agreement with the experimental observed trend, as in PhTzH, the N2—N3 distance is 1.247 Å, while in the PzTz⁻ anion, this bond lengthens to 1.283 Å. We note, in passing, that an interesting feature of the tetrazole ring is in preservation of the heterocycle aromaticity in its neutral, protonated and deprotonated forms.

The conformation of the diethylammonium is normal, with an sp^3 hybridized atom N5 and staggered conformations about the C—C and C—N bonds.

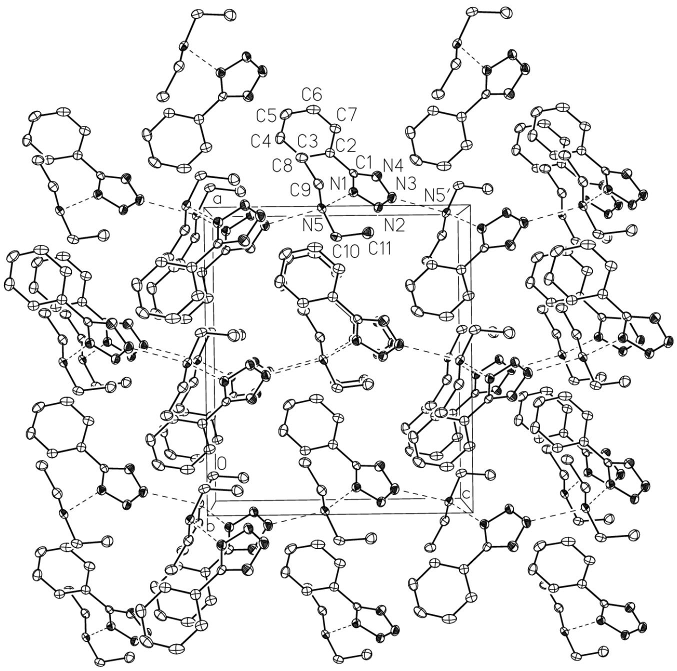


Figure 2
A molecular packing diagram of (I).

Experimental

Compound (I) is a side product of a synthesis which will be published soon (Guzei, 2002). The X-ray quality crystals of (I) were obtained by slow crystallization from a benzene/hexane solution mixture at room temperature. ^{1}H NMR (δ, p.p.m., C_6D_6, room temperature, 500 MHz): 1.09 (*t*, 6H, $J = 7.5$ Hz), 2.64 (*q*, 4H, $J = 7.5$ Hz), 7.12 (*t*, 1H, $J = 7.12$ Hz), 7.27 (*t*, 2H, $J = 7.8$ Hz), 8.49 (*d*, 2H, $J = 8.0$ Hz), 10.80 (*br s*, 2H).

Crystal data

$C_4H_{12}N^+\cdot C_7H_5N_4^-$
$M_r = 219.30$
Orthorhombic, $Pna2_1$
$a = 13.546$ (2) Å
$b = 7.6006$ (12) Å
$c = 11.6980$ (19) Å
$V = 1204.4$ (3) Å^3
$Z = 4$
$D_x = 1.209$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 6907 reflections
$\theta = 2$–$25°$
$\mu = 0.08$ mm^{-1}
$T = 100$ (2) K
Needle, colorless
0.50 × 0.10 × 0.10 mm

Data collection

Bruker CCD-1000 area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{\min} = 0.962$, $T_{\max} = 0.992$
8561 measured reflections

1236 independent reflections
1200 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 26.0°$
$h = -16 \rightarrow 16$
$k = -9 \rightarrow 9$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.107$
$S = 1.37$
1236 reflections
196 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 0.2756P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

N1—C1	1.345 (4)	N3—N4	1.348 (4)
N1—N2	1.346 (4)	N4—C1	1.327 (4)
N2—N3	1.308 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5B···N1	0.85 (4)	2.02 (4)	2.855 (4)	170 (3)
N5—H5A···N3^{i}	0.88 (4)	1.91 (5)	2.787 (4)	173 (3)

Symmetry code: (i) $2 - x, 1 - y, z - \frac{1}{2}$.

For the final refinement of the structure, the Friedel pairs were merged, as the use of Mo radiation on an organic crystal containing only light elements (nitrogen is the heaviest) does not allow unequivocal establishment of the absolute configuration.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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