

CRYSTALLOGRAPHIC
COMMUNICATIONS

OPEN ACCESS

ISSN 2056-9890

Crystal structure of 2-diazoimidazole-4,5-dicarbonitrile

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Received 4 May 2015; accepted 5 June 2015

Edited by A. M. Chippindale, University of Reading, England

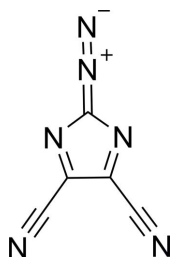
In the title compound, C₅N₆, all the atoms are approximately coplanar. In the crystal, molecules are packed with short contact distances of 2.885 (2) (between the diazo N atom connected to the ring and a cyano N atom on a neighboring molecule) and 3.012 (2) Å (between the terminal diazo N atom and an N atom of a neighboring imidazole ring).

Keywords: crystal structure; diazo; imidazole; carbonitrile.

CCDC reference: 1056377

1. Related literature

For synthesis of the title compound, see: Lu & Just (2001); Sheppard & Webster (1973). Few diazo-containing molecules have been isolated, and of these, only a small number have been examined by X-ray diffraction, see: Daidone *et al.* (2005); Dippold *et al.* (2012). The majority of these compounds are found as diazonium ions, rather than the neutral diazo species, see: Bugg *et al.* (1964).



2. Experimental

2.1. Crystal data

C₅N₆

M_r = 144.11

Trigonal, *P*3₂1
a = 8.0746 (3) Å
c = 16.7315 (6) Å
V = 944.73 (8) Å³
Z = 6

Mo *K*α radiation
μ = 0.11 mm^{−1}
T = 150 K
0.37 × 0.30 × 0.08 mm

2.2. Data collection

Bruker SMART APEXII CCD
diffractometer
Absorption correction: multi-scan
(*SADABS*; Bruker, 2008)
*T*_{min} = 0.930, *T*_{max} = 0.991

9178 measured reflections
1289 independent reflections
1269 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.019

2.3. Refinement

R [*F*² > 2σ(*F*²)] = 0.021
wR (*F*²) = 0.058
S = 1.09
1289 reflections

100 parameters
Δρ_{max} = 0.14 e Å^{−3}
Δρ_{min} = −0.11 e Å^{−3}

Data collection: *APEX2* (Bruker, 2009); cell refinement: *APEX2* and *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009) and *XPREF* (Bruker, 2008); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *CHEMDRAW Ultra* (Cambridge Soft, 2014).

Acknowledgements

Crystallographic studies were supported in part by the Office of Naval Research (ONR) (Award No. N00014-15-WX-0-0149). The authors would like to thank the Joint Munitions Technology Development Program for funding this work. Los Alamos National Laboratory is operated by Los Alamos National Security (LANS, LLC) under contract No. DE-AC52-06 N A25396 for the US Department of Energy (LA-UR-15-23325).

Supporting information for this paper is available from the IUCr electronic archives (Reference: CQ2016).

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supporting information

Acta Cryst. (2015). E71, o491 [doi:10.1107/S2056989015010944]

Crystal structure of 2-diazoimidazole-4,5-dicarbonitrile

Damon A. Parrish, Stephanie Kramer, G. Kenneth Windler, David E. Chavez and Philip W. Leonard

S1. Comment

Diazo moieties are ubiquitous in organic chemistry due to their ability to act as outstanding leaving groups in substitution reactions. This same reactivity also leads to their instability, and most are prone to decomposition, often violently. For this reason, few diazo-containing molecules have been isolated, and of these, only a small number have been examined by X-ray diffraction [Daidone *et al.* (2005), Dippold *et al.* (2012)]. The majority of these compounds are found as diazonium ions, rather than the neutral diazo species [Bugg *et al.* (1964)]. In contrast, the title compound has a neutral diazo moiety on C2 and is unusual in that it contains only carbon and nitrogen.

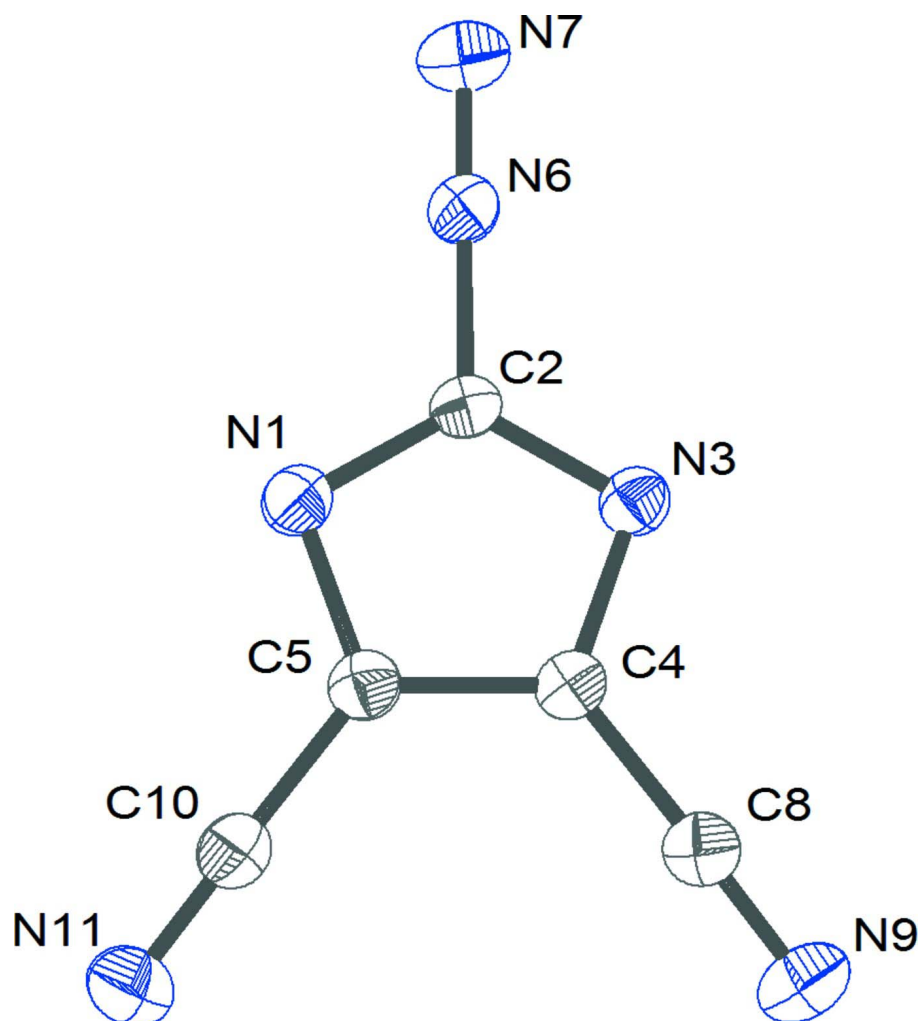
S2. Experimental

Caution! This compound can explode from slight friction, impact, or thermal shock. Although the explosion is not powerful, it is recommended that this material is only prepared in less than 5 gram quantities, handled wet, and not confined in any way.

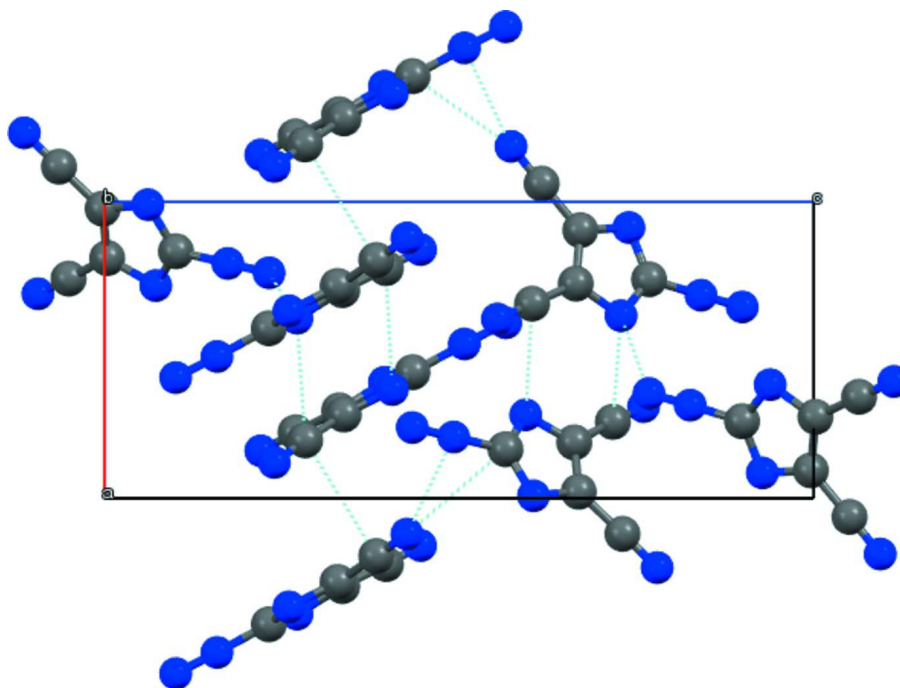
The title compound was prepared by the literature method (Lu and Just, 2001). Crystals were obtained by slow evaporation of a dilute aqueous solution of the title compound.

S3. Refinement

The Flack parameter initially refined to 0.3 (5). Before the final refinement cycle, this parameter was reset to zero and the Friedel pairs merged.

**Figure 1**

The molecular structure of the title compound (displacement ellipsoids are drawn at the 50% probability level).

**Figure 2**

A packing diagram of the title compound viewed along the *b* axis. Close contacts are represented by dashed lines.

2-Diazoimidazole-4,5-dicarbonitrile

Crystal data

C_5N_6

$M_r = 144.11$

Trigonal, $P3_221$

$a = 8.0746$ (3) Å

$c = 16.7315$ (6) Å

$V = 944.73$ (8) Å³

$Z = 6$

$F(000) = 432$

$D_x = 1.520$ Mg m⁻³

Melting point: 413 K (expl.) K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

$\mu = 0.11$ mm⁻¹

$T = 150$ K

Plate, purple

$0.37 \times 0.30 \times 0.08$ mm

Data collection

Bruker SMART APEXII CCD
diffractometer

Radiation source: fine focus sealed tube

ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2008)

$T_{\min} = 0.930$, $T_{\max} = 0.991$

9178 measured reflections

1289 independent reflections

1269 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 26.4^\circ$, $\theta_{\min} = 3.2^\circ$

$h = -10 \rightarrow 10$

$k = -10 \rightarrow 10$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.058$

$S = 1.09$

1289 reflections

100 parameters

0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 0.1041P]$
where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.11 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|-------------|----------------------------------|
| N1 | 0.61645 (16) | 0.00825 (16) | 0.93835 (6) | 0.0254 (3) |
| C2 | 0.7396 (2) | 0.16549 (19) | 0.89882 (7) | 0.0226 (3) |
| N3 | 0.91448 (16) | 0.28157 (17) | 0.92732 (6) | 0.0239 (3) |
| C4 | 0.90565 (19) | 0.18858 (19) | 0.99570 (7) | 0.0225 (3) |
| C5 | 0.72502 (19) | 0.02197 (19) | 1.00215 (7) | 0.0240 (3) |
| N6 | 0.68567 (16) | 0.20682 (16) | 0.82574 (6) | 0.0238 (3) |
| N7 | 0.6461 (2) | 0.23873 (19) | 0.76756 (7) | 0.0329 (3) |
| C8 | 1.0629 (2) | 0.2582 (2) | 1.05016 (7) | 0.0258 (3) |
| N9 | 1.18839 (19) | 0.3094 (2) | 1.09341 (7) | 0.0351 (3) |
| C10 | 0.6572 (2) | −0.1202 (2) | 1.06366 (8) | 0.0299 (3) |
| N11 | 0.6055 (2) | −0.2345 (2) | 1.11254 (8) | 0.0441 (4) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|------------|-------------|-------------|
| N1 | 0.0235 (6) | 0.0266 (6) | 0.0250 (5) | 0.0117 (5) | −0.0016 (4) | −0.0005 (5) |
| C2 | 0.0241 (6) | 0.0255 (6) | 0.0200 (5) | 0.0138 (5) | −0.0021 (5) | −0.0011 (5) |
| N3 | 0.0234 (6) | 0.0258 (6) | 0.0226 (5) | 0.0125 (5) | −0.0006 (4) | −0.0012 (4) |
| C4 | 0.0223 (6) | 0.0251 (6) | 0.0223 (6) | 0.0135 (5) | −0.0002 (5) | −0.0022 (5) |
| C5 | 0.0237 (6) | 0.0266 (6) | 0.0237 (6) | 0.0140 (6) | 0.0002 (4) | −0.0005 (5) |
| N6 | 0.0231 (6) | 0.0256 (6) | 0.0244 (5) | 0.0136 (5) | −0.0005 (4) | −0.0020 (4) |
| N7 | 0.0370 (7) | 0.0425 (8) | 0.0282 (6) | 0.0265 (6) | −0.0027 (5) | −0.0003 (5) |
| C8 | 0.0266 (7) | 0.0298 (7) | 0.0239 (6) | 0.0161 (6) | 0.0024 (5) | −0.0005 (5) |
| N9 | 0.0310 (7) | 0.0467 (8) | 0.0306 (6) | 0.0216 (6) | −0.0070 (5) | −0.0064 (5) |
| C10 | 0.0240 (7) | 0.0324 (7) | 0.0314 (7) | 0.0127 (6) | −0.0020 (5) | 0.0025 (6) |
| N11 | 0.0362 (7) | 0.0456 (8) | 0.0451 (8) | 0.0164 (7) | −0.0007 (6) | 0.0179 (6) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|-------|-------------|--------|-------------|
| N1—C2 | 1.3327 (18) | C4—C8 | 1.4297 (18) |
| N1—C5 | 1.3502 (16) | C5—C10 | 1.4314 (18) |
| C2—N3 | 1.3325 (18) | N6—N7 | 1.0946 (15) |
| C2—N6 | 1.3936 (15) | C8—N9 | 1.1415 (19) |

| | | | |
|-------------|--------------|--------------|--------------|
| N3—C4 | 1.3507 (17) | C10—N11 | 1.144 (2) |
| C4—C5 | 1.4094 (18) | | |
| C2—N1—C5 | 99.75 (11) | C5—C4—C8 | 128.18 (12) |
| N3—C2—N1 | 121.08 (11) | N1—C5—C4 | 109.72 (11) |
| N3—C2—N6 | 119.59 (12) | N1—C5—C10 | 122.03 (12) |
| N1—C2—N6 | 119.33 (12) | C4—C5—C10 | 128.23 (12) |
| C2—N3—C4 | 99.74 (11) | N7—N6—C2 | 178.50 (12) |
| N3—C4—C5 | 109.70 (11) | N9—C8—C4 | 178.23 (16) |
| N3—C4—C8 | 122.12 (13) | N11—C10—C5 | 178.82 (17) |
| C5—N1—C2—N3 | −0.01 (16) | C2—N1—C5—C4 | 0.36 (14) |
| C5—N1—C2—N6 | 178.72 (11) | C2—N1—C5—C10 | −178.37 (13) |
| N1—C2—N3—C4 | −0.34 (16) | N3—C4—C5—N1 | −0.61 (16) |
| N6—C2—N3—C4 | −179.07 (11) | C8—C4—C5—N1 | 179.57 (12) |
| C2—N3—C4—C5 | 0.53 (14) | N3—C4—C5—C10 | 178.02 (13) |
| C2—N3—C4—C8 | −179.64 (12) | C8—C4—C5—C10 | −1.8 (2) |
