

**Keywords:** crystal structure; substituted 2-azabuta-1,3-diene; weak hydrogen bonding; halogen bonding;  $\pi$ - $\pi$  interactions.

**CCDC reference:** 1491488

**Supporting information:** this article has supporting information at journals.iucr.org/e

# Crystal structure of 4,4-dibromo-1-(3,4-dimethoxyphenyl)-2-azabuta-1,3-diene-1-carbonitrile

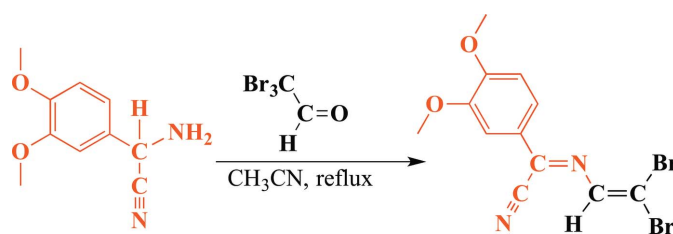
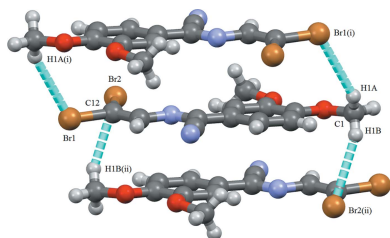
Marwa Chaabene,<sup>a</sup> Abderrahim Khatyr,<sup>b</sup> Michael Knorr,<sup>b\*</sup> Moheddine Askri,<sup>a</sup> Yoann Rousselin<sup>c</sup> and Marek M. Kubicki<sup>c\*</sup>

<sup>a</sup>Laboratoire de Chimie Hétérocyclique, Produits Naturels et Réactivité (LR11ES39), Département de Chimie, Faculté des Sciences de Monastir, Tunisia, <sup>b</sup>Institut UTINAM UMR CNRS 6213, University of Franche-Comté, 16 route de Gray, 25030 Besançon, France, and <sup>c</sup>ICMUB UMR CNRS 6302, University of Bourgogne, 9 avenue Alain Savary, 21078 Dijon, France. \*Correspondence e-mail: michael.knorr@univ-fcomte.fr, marek.kubicki@u-bourgogne.fr

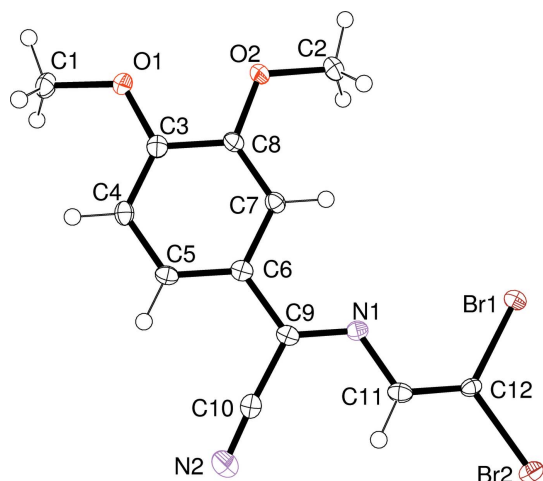
The title compound, C<sub>12</sub>H<sub>10</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>, represents an example of a planar  $\pi$ -conjugated 2-azabutadiene molecule, which is both an interesting starting material for further organic transformations and a potential ligand in organometallic coordination chemistry. Its metric molecular parameters are typical for the family of 2-azabuta-1,3-dienes not substituted at the (CH) 3-position. In the crystal, the almost planar (r.m.s. deviation = 0.0658 Å) azadiene molecules form one-dimensional double-wide ribbons through intermolecular halogen bonds (C—Br $\cdots$ O and C—Br $\cdots$ Br—C), which then stack in a slipped manner through weak C—H $\cdots$ Br and  $\pi$ - $\pi$  interactions to generate a three-dimensional network.

## 1. Chemical context

In the context of our interest in developing novel  $\pi$ -conjugated dithioether compounds as ligands for coordination chemistry and further organic transformations, we have reported on the synthesis and crystal structure of 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene [Ph<sub>2</sub>C=N—C(H)=CCl<sub>2</sub>] and its conversion to [Ph<sub>2</sub>C=N—C(H)=C(SR)<sub>2</sub>] and [Ph<sub>2</sub>C=N—C(H)=C(OPh)<sub>2</sub>] by reaction with thiolates NaSR or NaOPh, respectively (Jacquot *et al.*, 1999, 2000; Jacquot-Rousseau *et al.*, 2006; Kinghat *et al.*, 2016). Several crystal structures of these molecules/ligands and their derived transition metal complexes reveal that despite the overall planarity of the  $\pi$ -conjugated chain, one aryl group of the —N=CPh<sub>2</sub> imine segment is tilted with respect to the azabutadienic array (Jacquot *et al.*, 1999; Knorr *et al.*, 2003; Kinghat *et al.*, 2008). To circumvent this feature and to modulate the stereoelectronic properties, we examined other synthetic strategies for the synthesis of 2-azabutadienes. Intrigued by a communication briefly mentioning the formation of the nitrile-functionalized compounds [Ph(C $\equiv$ N)C=N—C(H)=CX<sub>2</sub>] (X = Cl or Br) by treatment of the

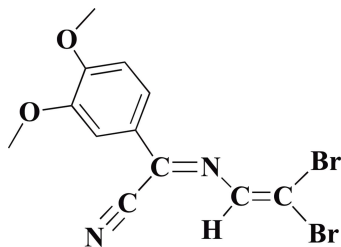


**Figure 1**  
The reaction scheme for the synthesis of (1).



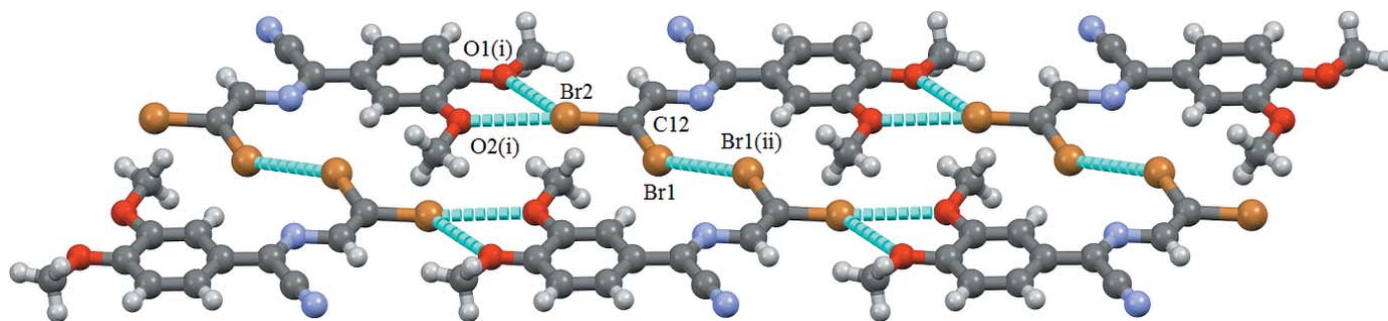
**Figure 2**  
An displacement ellipsoid plot of (1) at the 50% probability level.

$\alpha$ -aminonitrile  $\text{H}_2\text{NCHPhC}\equiv\text{N}$  with chloral or bromal (Sato & Adachi, 1978), we reinvestigated this reaction to explore the scope for the synthesis of other derivatives. For example, we succeeded in preparing the title compound  $[\text{C}_6\text{H}_3(\text{OMe})_2(\text{C}\equiv\text{N})\text{C}=\text{N}-\text{C}(\text{H})=\text{CBr}_2]$ , (1), bearing two electron-donating methoxy groups at the *meta*- and *para*-positions of the aryl ring (see Fig. 1).



## 2. Structural commentary

Compound (1) crystallizes from acetonitrile in the triclinic crystal system, space group  $P\bar{1}$ . The *transoid* conformation of the azabutadiene chain found in  $[\text{Ph}_2\text{C}=\text{N}-\text{C}(\text{H})=\text{CCl}_2]$  (Jacquot *et al.*, 1999) is also observed in the crystal structure of (1) (Fig. 2). The azadiene chain (C9/N1/C11/C12) is essentially



**Figure 3**  
Part of the crystal structure of (1), showing the formation of double-wide ribbons through halogen  $\text{C}-\text{Br}\cdots\text{O}$  and  $\text{C}-\text{Br}\cdots\text{Br}-\text{C}$  bonding. [Symmetry codes: (i)  $x - 1, y, z - 1$ ; (ii)  $-x + 1, -y + 2, -z + 1$ .]

**Table 1**  
Halogen-bonding parameters ( $\text{\AA}$ ,  $^\circ$ ) for (1).

<i>D</i>	Br	<i>A</i>	<i>D</i> –Br	Br $\cdots$ <i>A</i>	<i>D</i> –Br $\cdots$ <i>A</i>
C12	Br2	O1 <sup>i</sup>	1.878 (3)	3.185 (2)	124.26 (9)
C12	Br2	O2 <sup>i</sup>	1.878 (3)	3.153 (2)	167.6 (1)
C12	Br1	Br1 <sup>ii</sup>	1.872 (3)	3.4340 (5)	144.8 (1)

Symmetry codes: (i)  $x - 1, y, z - 1$ ; (ii)  $-x + 1, -y + 2, -z + 1$ .

**Table 2**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

<i>D</i> –H $\cdots$ <i>A</i>	<i>D</i> –H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> –H $\cdots$ <i>A</i>
C1–H1A $\cdots$ Br1 <sup>i</sup>	0.98	3.01	3.867 (4)	146
C1–H1B $\cdots$ Br2 <sup>ii</sup>	0.98	3.04	3.869 (4)	143

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x, -y + 1, -z + 1$ .

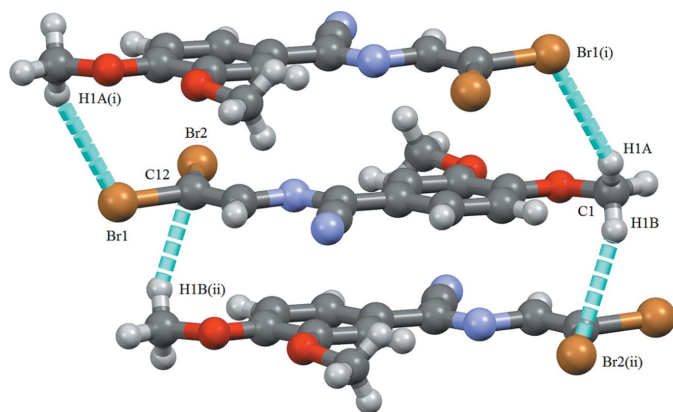
planar (r.m.s. deviation = 0.014  $\text{\AA}$ ). The torsion angle C12–C11–N1–C9 is 177.9 (3) $^\circ$ . The aryl ring, as well as the CN substituent, form part of the  $\pi$ -conjugated array. The length of the vinylic C11=C12 bond matches well with that of  $[\text{Ph}_2\text{C}=\text{N}-\text{C}(\text{H})=\text{CCl}_2]$  [1.332 (4) *versus* 1.319 (3)  $\text{\AA}$ ]. We are not aware of any other structurally characterized azabutadienes bearing a  $\text{Br}_2\text{C}=\text{C}$  moiety. For other organic compounds containing this dibromovinyl unit, such as 2,2-dibromovinylthiophene and 2-(2,2-dibromovinyl)-1-methyl-1*H*-imidazole-4,5-dicarbonitrile, C=C distances of 1.335 (7) and 1.317 (3)  $\text{\AA}$  have been reported (Clément *et al.*, 2011; Lokaj *et al.*, 2011). The C9=N1 bond length of the imine group is also comparable with that of  $[\text{Ph}_2\text{C}=\text{N}-\text{C}(\text{H})=\text{CCl}_2]$  [1.288 (3) *versus* 1.293 (2)  $\text{\AA}$ ].

## 3. Supramolecular features

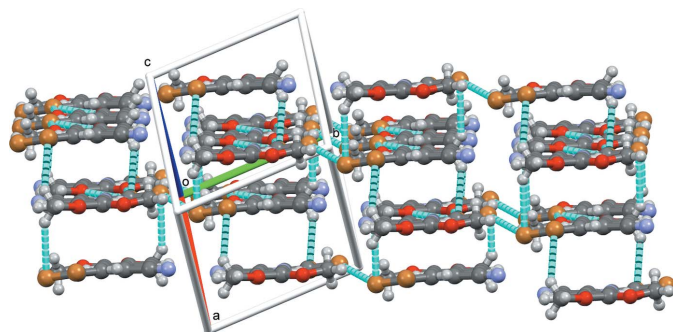
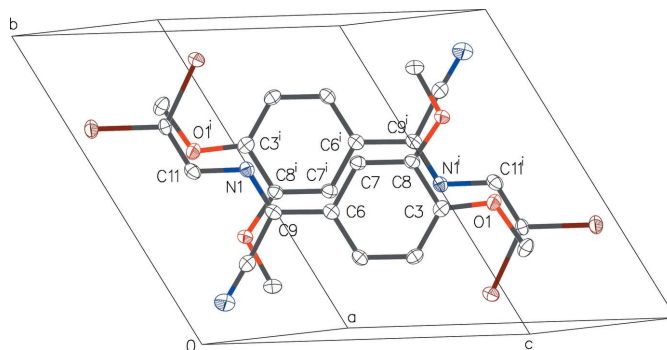
Each planar molecule of (1) is connected through halogen (Cavallo *et al.*, 2016) bifurcated bonds C12–Br2 $\cdots$ (O1,O2) to two neighbouring molecules to form a one-dimensional ribbon. The ribbon is further connected through another kind of side halogen bond (C12–Br1 $\cdots$ Br1–C12) to other neighbouring molecules with the formation of roughly planar one-dimensional double-wide straight chains (Fig. 3 and Table 1). These chains then stack in a slipped manner through

**Table 3**  
 $\pi$ - $\pi$  interactions ( $\text{\AA}$ ) in (1).

Atom A	Atom B	$A \cdots B$	Atom C	Atom D	$C \cdots D$
C5	C12 <sup>ii</sup>	3.445 (5)	C11	O1 <sup>i</sup>	3.455 (4)
C6	C11 <sup>ii</sup>	3.497 (5)	N1	C3 <sup>i</sup>	3.556 (4)
C9	N1 <sup>ii</sup>	3.451 (4)	C9	C8 <sup>i</sup>	3.523 (5)
			C6	C7 <sup>i</sup>	3.559 (5)

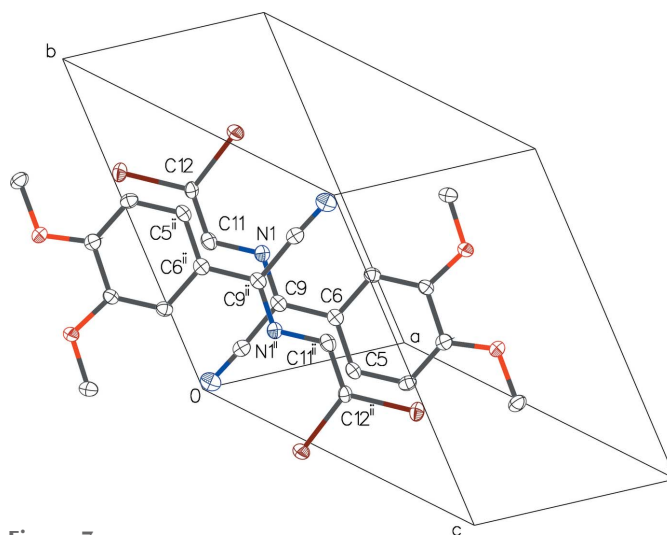
 Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $-x, 1 - y, 1 - z$ .

**Figure 4**  
 Part of the crystal structure of (1), showing the C—H...Br interactions. [Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x, -y + 1, -z + 1$ .]

very weak C—H...Br interactions (Fig. 4 and Table 2) to generate a three-dimensional supramolecular network (Fig. 5). When projecting the structure down the direction perpendicular to the planes of the planar molecules of (1) (e.g. down from the top in Fig. 4), one sees an interesting overlap in a head-to-tail arrangement of zigzagging unsaturated chains that leads to the formation of  $\pi$ - $\pi$  stacking interactions around the symmetry centres located at  $(0, \frac{1}{2}, \frac{1}{2})$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . They consist of overlaps between the azadiene C=C and C=N double bonds and parts of the aryl rings. For clarity, these overlaps are shown separately in Figs. 6 and 7. The mean interatomic separation between the chains built around  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  (Fig. 6 and Table 3) is 3.523 (5)  $\text{\AA}$ , while a slightly shorter separation of 3.464 (5)  $\text{\AA}$  is observed for the second couple built around  $(0, \frac{1}{2}, \frac{1}{2})$  (Fig. 7 and Table 3).


**Figure 5**  
 Part of the three-dimensional packing in (1) projected down the [101] direction and showing the halogen and weak C—H...Br interactions detailed in Figs. 3 and 4.

**Figure 6**  
 Part of the crystal structure of (1), showing the potential  $\pi$ - $\pi$  interactions in two head-to-tail molecules overlapping around the symmetry centre at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  (see also Fig. 4). H atoms have been omitted for clarity. [Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .]

#### 4. Database survey

There are several other examples of structurally characterized 2-azabutadienes bearing cyano (nitrile) substituents attached at the azabutadienic array. These include 3-cyano-4-(*n*-methoxyphenyl)-1,1-diphenyl-2-aza-1,3-butadienes ( $n = 2, 3$  or 4), 3-cyano-4-(4-cyanophenyl)-1,1-diphenyl-2-aza-1,3-butadiene, 3-cyano-4-(2,4-dimethoxyphenyl)-1,1-diphenyl-2-aza-1,3-butadiene, 3-cyano-4-(2,4-dichlorophenyl)-1,1-diphenyl-2-aza-1,3-butadiene and 3-cyano-4-(*n*-fluorophenyl)-1,1-diphenyl-2-aza-1,3-butadienes ( $n = 2$  or 4) (Angelova *et al.*, 1993*a,b*; Macicek *et al.*, 1993*a,b*; Dryanska *et al.*, 1995). Furthermore, the structure of (*E*)-4,4-dicyano-3-methylthio-1-phenyl-1-(1-pyrrolidinyl)-2-azabuta-1,3-diene has been reported (Lorente *et al.*, 1996). Note that in all these structures there is a significant deviation from linearity of the C=N—C=C chain. This feature is due to the presence of a substituent at the 3-C position of the 2-azabuta-1,3-diene chain. We also observed


**Figure 7**  
 Part of the crystal structure of (1), showing the potential  $\pi$ - $\pi$  interactions in two head-to-tail molecules overlapping around the symmetry centre at  $(0, \frac{1}{2}, \frac{1}{2})$  (see also Fig. 4). H atoms have been omitted for clarity. [Symmetry code: (ii)  $-x, -y + 1, -z + 1$ .]

and discussed this feature in the structures of [Ar<sub>2</sub>C=N—C(S<sup>t</sup>Bu)=C(H)S<sup>t</sup>Bu] (Kinghat *et al.*, 2016).

### 5. Synthesis and crystallization

The required  $\alpha$ -aminonitrile used a starting material was obtained according a literature protocol (Mai & Patil, 1984). An equimolar mixture of *N*-(dibromoethylenyl)-1-imino-1-vertracetonitrile (10 mmol) and tribromoacetaldehyde in 10 ml of acetonitrile was stirred under reflux for 2 h. The solution was then filtered and all volatiles removed under reduced pressure. The crude residue was recrystallized from acetonitrile affording clear-light orange crystals (yield 79%; m.p. 440 K; <sup>1</sup>H RMN (CDCl<sub>3</sub>, 300 MHz):  $\delta$  3.95 (*s*, 3H, OCH<sub>3</sub>), 3.96 (*s*, 3H, OCH<sub>3</sub>), 6.93 (*d*, 1H, *J* = 9 Hz, 1 Ar-H), 7.65 (*s*, 2H, 2 Ar-H), 8.04 (*s*, 1H, =CH); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  55.9 (OCH<sub>3</sub>), 56.2 (OCH<sub>3</sub>), 103.2 (=CBr<sub>2</sub>), 110.6 (C $\equiv$ N), 124.3–153.9 (C<sub>Ar</sub>), 137.8 (C=N), 142.2 (CH);  $\lambda_{\max}$  = 245 nm ( $\epsilon$  = 3300 M<sup>-1</sup> cm<sup>-1</sup>),  $\lambda_{\max}$  = 353 nm ( $\epsilon$  = 7580 M<sup>-1</sup> cm<sup>-1</sup>); IR (ATR) cm<sup>-1</sup>: 2219 (C $\equiv$ N), 1597 (C=N), 1569 (C=C).

### 6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 4. All H atoms were placed in calculated positions and treated in a riding model. C—H distances were set at 0.95 (aromatic) and 0.98 Å (methyl), with  $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$ , where  $x = 1.5$  for idealized methyl H atoms refined as rotating groups and 1.2 for all other H atoms.

### Acknowledgements

We are grateful to the Universities of Franche-Comté and Bourgogne and the CNRS for financial support.

### References

Angelova, O., Macíček, J. & Dryanska, V. (1993a). *Acta Cryst.* **C49**, 1813–1818.  
 Angelova, O., Macíček, J. & Dryanska, V. (1993b). *Acta Cryst.* **C49**, 1821–1823.  
 Bruker (2013). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Bruker (2014). *APEX2* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Cavallo, G., Metrangolo, P., Milani, R., Pilati, T., Priimagi, A., Resnati, G. & Terraneo, G. (2016). *Chem. Rev.* **116**, 2478–2601.  
 Clément, S., Guyard, L., Knorr, M., Eckert, P. K. & Strohmman, C. (2011). *Acta Cryst.* **E67**, o481.  
 Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.  
 Dryanska, V., Angelova, O., Macicek, J., Shishkova, L., Denkova, P. & Spassov, S. (1995). *J. Chem. Res.* pp. 268–269.  
 Jacquot, S., Belaissaoui, A., Schmitt, G., Laude, B., Kubicki, M. M. & Blacque, O. (1999). *Eur. J. Org. Chem.* pp. 1541–1544.

**Table 4**  
Experimental details.

Crystal data	
Chemical formula	C <sub>12</sub> H <sub>10</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub>
<i>M<sub>r</sub></i>	374.04
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.6878 (4), 9.2782 (5), 10.8111 (6)
$\alpha$ , $\beta$ , $\gamma$ (°)	106.162 (2), 100.887 (2), 110.009 (2)
<i>V</i> (Å <sup>3</sup> )	660.57 (6)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	6.13
Crystal size (mm)	0.25 × 0.2 × 0.1
Data collection	
Diffractometer	Bruker D8 VENTURE
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2014)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.537, 0.746
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	23955, 3045, 2442
<i>R<sub>int</sub></i>	0.067
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.652
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.027, 0.067, 1.03
No. of reflections	3045
No. of parameters	165
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.80, -0.42

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

Jacquot, S., Schmitt, G., Laude, B., Kubicki, M. M. & Blacque, O. (2000). *Eur. J. Org. Chem.* pp. 1235–1239.  
 Jacquot-Rousseau, S., Schmitt, G., Khatyr, A., Knorr, M., Kubicki, M. M., Vigier, E. & Blacque, O. (2006). *Eur. J. Org. Chem.* pp. 2748–2751.  
 Kinghat, R., Boudiba, H., Khatyr, A., Knorr, M. & Kubicki, M. M. (2008). *Acta Cryst.* **E64**, o370.  
 Kinghat, R., Schmitt, G., Ciamala, K., Khatyr, A., Knorr, M., Jacquot-Rousseau, S., Rousselin, Y. & Kubicki, M. M. (2016). *C. R. Chim.* **19**, 319–331.  
 Knorr, M., Schmitt, G., Kubicki, M. M. & Vigier, E. (2003). *Eur. J. Inorg. Chem.* pp. 514–517.  
 Lokaj, J., Moncol, J., Bures, F. & Kulhanek, J. (2011). *J. Chem. Crystallogr.* **41**, 834–837.  
 Lorente, A., Casillas, M., Gomez-Sal, P. & Manzanero, A. (1996). *Can. J. Chem.* **74**, 287–294.  
 Macíček, J., Angelova, O. & Dryanska, V. (1993a). *Acta Cryst.* **C49**, 1818–1821.  
 Macíček, J., Angelova, O. & Dryanska, V. (1993b). *Acta Cryst.* **C49**, 2169–2173.  
 Mai, K. & Patil, G. (1984). *Tetrahedron Lett.* **25**, 4583–4586.  
 Sato, N. & Adachi, J. (1978). *J. Org. Chem.* **43**, 340–341.  
 Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.  
 Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.

## supporting information

*Acta Cryst.* (2016). E72, 1167-1170 [https://doi.org/10.1107/S2056989016011075]

## Crystal structure of 4,4-dibromo-1-(3,4-dimethoxyphenyl)-2-azabuta-1,3-diene-1-carbonitrile

Marwa Chaabene, Abderrahim Khatyr, Michael Knorr, Moheddine Askri, Yoann Rousselin and Marek M. Kubicki

### Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *S SAINT* (Bruker, 2013); data reduction: *S SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### 4,4-Dibromo-1-(3,4-dimethoxyphenyl)-2-azabuta-1,3-diene-1-carbonitrile

#### Crystal data

$C_{12}H_{10}Br_2N_2O_2$

$M_r = 374.04$

Triclinic,  $P\bar{1}$

$a = 7.6878$  (4) Å

$b = 9.2782$  (5) Å

$c = 10.8111$  (6) Å

$\alpha = 106.162$  (2)°

$\beta = 100.887$  (2)°

$\gamma = 110.009$  (2)°

$V = 660.57$  (6) Å<sup>3</sup>

$Z = 2$

$F(000) = 364$

$D_x = 1.881$  Mg m<sup>-3</sup>

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

Cell parameters from 8732 reflections

$\theta = 3.0$ – $27.5$ °

$\mu = 6.13$  mm<sup>-1</sup>

$T = 100$  K

Plqte, clear light orange

$0.25 \times 0.2 \times 0.1$  mm

#### Data collection

Bruker D8 VENTURE

diffractometer

Radiation source: X-ray tube, Siemens KFF Mo

2K-90C

TRIUMPH curved crystal monochromator

$\varphi$  and  $\omega$  scans'

Absorption correction: multi-scan

(SADABS; Bruker, 2014)

$T_{\min} = 0.537$ ,  $T_{\max} = 0.746$

23955 measured reflections

3045 independent reflections

2442 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.067$

$\theta_{\max} = 27.6$ °,  $\theta_{\min} = 3.0$ °

$h = -9 \rightarrow 10$

$k = -12 \rightarrow 12$

$l = -14 \rightarrow 14$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.067$

$S = 1.03$

3045 reflections

165 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 0.5386P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.80 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$

#### Special details

**Experimental.** Absorption correction: SADABS-2014/4 (Bruker,2014) was used for absorption correction. wR2(int) was 0.0938 before and 0.0647 after correction. The Ratio of minimum to maximum transmission is 0.7197. The  $\lambda/2$  correction factor is 0.00150.

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

#### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5229 (4)	0.2556 (4)	0.9031 (3)	0.0198 (6)
H1A	0.5402	0.1716	0.8346	0.030*
H1B	0.3876	0.2129	0.9037	0.030*
H1C	0.6109	0.2824	0.9927	0.030*
C2	0.6815 (5)	0.8341 (4)	0.8299 (3)	0.0246 (7)
H2A	0.7114	0.8389	0.7465	0.037*
H2B	0.7909	0.9196	0.9088	0.037*
H2C	0.5636	0.8527	0.8307	0.037*
C3	0.4518 (4)	0.3908 (3)	0.7558 (3)	0.0163 (6)
C4	0.3008 (4)	0.2473 (3)	0.6590 (3)	0.0160 (6)
H4	0.2729	0.1450	0.6709	0.019*
C5	0.1904 (4)	0.2535 (3)	0.5444 (3)	0.0156 (6)
H5	0.0857	0.1552	0.4792	0.019*
C6	0.2308 (4)	0.4007 (3)	0.5242 (3)	0.0149 (5)
C7	0.3852 (4)	0.5476 (3)	0.6221 (3)	0.0154 (6)
H7	0.4130	0.6496	0.6096	0.019*
C8	0.4946 (4)	0.5419 (3)	0.7352 (3)	0.0149 (5)
C9	0.1186 (4)	0.4092 (3)	0.4029 (3)	0.0148 (5)
C10	-0.0396 (4)	0.2543 (4)	0.3038 (3)	0.0210 (6)
C11	0.0555 (4)	0.5495 (3)	0.2655 (3)	0.0175 (6)
H11	-0.0400	0.4495	0.1958	0.021*
C12	0.0911 (4)	0.6927 (3)	0.2490 (3)	0.0139 (5)
N1	0.1576 (3)	0.5463 (3)	0.3839 (2)	0.0145 (5)
N2	-0.1661 (4)	0.1374 (3)	0.2229 (3)	0.0356 (7)
O1	0.5666 (3)	0.4013 (2)	0.8715 (2)	0.0195 (4)
O2	0.6500 (3)	0.6752 (2)	0.8351 (2)	0.0195 (4)
Br1	0.27146 (4)	0.89631 (3)	0.38235 (3)	0.01976 (9)
Br2	-0.04365 (4)	0.69810 (3)	0.08743 (3)	0.01900 (9)

#### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0209 (14)	0.0221 (14)	0.0233 (16)	0.0103 (12)	0.0097 (12)	0.0148 (13)

C2	0.0258 (16)	0.0142 (14)	0.0254 (17)	0.0023 (12)	0.0012 (13)	0.0074 (13)
C3	0.0145 (13)	0.0177 (14)	0.0202 (15)	0.0082 (11)	0.0082 (11)	0.0086 (12)
C4	0.0180 (14)	0.0152 (13)	0.0194 (15)	0.0087 (11)	0.0095 (12)	0.0083 (11)
C5	0.0121 (13)	0.0167 (13)	0.0147 (14)	0.0043 (11)	0.0038 (11)	0.0035 (11)
C6	0.0142 (12)	0.0161 (13)	0.0146 (14)	0.0071 (10)	0.0062 (11)	0.0038 (11)
C7	0.0168 (13)	0.0137 (13)	0.0144 (14)	0.0050 (11)	0.0058 (11)	0.0044 (11)
C8	0.0132 (13)	0.0142 (13)	0.0152 (14)	0.0039 (10)	0.0046 (11)	0.0048 (11)
C9	0.0133 (13)	0.0151 (13)	0.0146 (14)	0.0061 (10)	0.0055 (11)	0.0025 (11)
C10	0.0226 (15)	0.0186 (14)	0.0217 (16)	0.0076 (13)	0.0050 (13)	0.0099 (13)
C11	0.0171 (14)	0.0170 (14)	0.0141 (14)	0.0069 (11)	0.0033 (11)	0.0012 (11)
C12	0.0133 (12)	0.0179 (13)	0.0104 (13)	0.0064 (11)	0.0042 (11)	0.0053 (11)
N1	0.0157 (11)	0.0160 (11)	0.0117 (12)	0.0072 (9)	0.0049 (9)	0.0038 (9)
N2	0.0337 (16)	0.0205 (14)	0.0371 (18)	0.0036 (12)	-0.0042 (14)	0.0087 (13)
O1	0.0191 (10)	0.0185 (10)	0.0202 (11)	0.0059 (8)	0.0025 (8)	0.0110 (9)
O2	0.0203 (10)	0.0130 (9)	0.0174 (11)	0.0017 (8)	-0.0006 (8)	0.0053 (8)
Br1	0.02102 (15)	0.01428 (14)	0.01661 (16)	0.00322 (11)	0.00125 (12)	0.00357 (11)
Br2	0.02026 (15)	0.02270 (16)	0.01424 (16)	0.01035 (12)	0.00265 (12)	0.00730 (12)

*Geometric parameters (Å, °)*

C1—H1A	0.9800	C5—C6	1.383 (4)
C1—H1B	0.9800	C6—C7	1.415 (4)
C1—H1C	0.9800	C6—C9	1.464 (4)
C1—O1	1.431 (3)	C7—H7	0.9500
C2—H2A	0.9800	C7—C8	1.372 (4)
C2—H2B	0.9800	C8—O2	1.372 (3)
C2—H2C	0.9800	C9—C10	1.465 (4)
C2—O2	1.430 (3)	C9—N1	1.288 (3)
C3—C4	1.387 (4)	C10—N2	1.147 (4)
C3—C8	1.418 (4)	C11—H11	0.9500
C3—O1	1.345 (3)	C11—C12	1.332 (4)
C4—H4	0.9500	C11—N1	1.384 (4)
C4—C5	1.391 (4)	C12—Br1	1.872 (3)
C5—H5	0.9500	C12—Br2	1.878 (3)
H1A—C1—H1B	109.5	C5—C6—C9	121.7 (2)
H1A—C1—H1C	109.5	C7—C6—C9	118.7 (2)
H1B—C1—H1C	109.5	C6—C7—H7	120.2
O1—C1—H1A	109.5	C8—C7—C6	119.6 (3)
O1—C1—H1B	109.5	C8—C7—H7	120.2
O1—C1—H1C	109.5	C7—C8—C3	120.5 (3)
H2A—C2—H2B	109.5	O2—C8—C3	114.7 (2)
H2A—C2—H2C	109.5	O2—C8—C7	124.8 (2)
H2B—C2—H2C	109.5	C6—C9—C10	117.0 (2)
O2—C2—H2A	109.5	N1—C9—C6	121.6 (2)
O2—C2—H2B	109.5	N1—C9—C10	121.5 (3)
O2—C2—H2C	109.5	N2—C10—C9	176.7 (3)
C4—C3—C8	119.4 (3)	C12—C11—H11	120.0

O1—C3—C4	125.4 (3)	C12—C11—N1	120.0 (3)
O1—C3—C8	115.1 (2)	N1—C11—H11	120.0
C3—C4—H4	120.1	C11—C12—Br1	123.0 (2)
C3—C4—C5	119.8 (3)	C11—C12—Br2	120.4 (2)
C5—C4—H4	120.1	Br1—C12—Br2	116.65 (14)
C4—C5—H5	119.5	C9—N1—C11	120.4 (2)
C6—C5—C4	120.9 (3)	C3—O1—C1	118.0 (2)
C6—C5—H5	119.5	C8—O2—C2	116.8 (2)
C5—C6—C7	119.6 (3)		
C3—C4—C5—C6	1.1 (4)	C7—C6—C9—C10	179.8 (2)
C3—C8—O2—C2	-171.0 (2)	C7—C6—C9—N1	0.0 (4)
C4—C3—C8—C7	1.5 (4)	C7—C8—O2—C2	9.3 (4)
C4—C3—C8—O2	-178.2 (2)	C8—C3—C4—C5	-1.4 (4)
C4—C3—O1—C1	-4.4 (4)	C8—C3—O1—C1	175.8 (2)
C4—C5—C6—C7	-0.7 (4)	C9—C6—C7—C8	-178.7 (2)
C4—C5—C6—C9	178.7 (3)	C10—C9—N1—C11	-2.9 (4)
C5—C6—C7—C8	0.8 (4)	C12—C11—N1—C9	177.2 (3)
C5—C6—C9—C10	0.3 (4)	N1—C11—C12—Br1	-1.7 (4)
C5—C6—C9—N1	-179.5 (3)	N1—C11—C12—Br2	179.0 (2)
C6—C7—C8—C3	-1.2 (4)	O1—C3—C4—C5	178.8 (3)
C6—C7—C8—O2	178.5 (2)	O1—C3—C8—C7	-178.7 (3)
C6—C9—N1—C11	176.9 (2)	O1—C3—C8—O2	1.5 (4)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C1—H1 <i>A</i> ...Br1 <sup>i</sup>	0.98	3.01	3.867 (4)	146
C1—H1 <i>B</i> ...Br2 <sup>ii</sup>	0.98	3.04	3.869 (4)	143

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $-x, -y+1, -z+1$ .