

## Synthesis and Crystal Structure of a 1,3-Bis(2-cyanophenyl)triazene Hydrogen-Bonded Compound

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The crystal structure of the title compound, 1,3-bis(2-cyanophenyl)triazene, shows a dimer formation between two molecules of L through intermolecular hydrogen bonds D-H... (A1, A1'). The directions of the aromatic rings indicate the presence of strong face-to-face  $\pi$ - $\pi$  stacking interactions and intermolecular C-H...N hydrogen bonds. These interactions extend the two-dimensional chains further into a three-dimensional network.

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1,3-Diaryltriazenes are a unique class of polyazo compounds containing three consecutive nitrogen atoms in an acyclic arrangement and a proton linked to one of them. Aryl triazenes have been studied for over 130 years concerning their interesting structural, anticancer, and reactivity properties.<sup>1</sup> Triazenes with an available proton on a nitrogen atom are able to undergo hydrogen bonding. 1,3-Diaryltriazenes, on the other hand, are able to participate in face-to-face and edge-to-face  $\pi$ -stacking interactions to form a very stable layered structure, like a polymer. In this work, we report on the synthesis and crystal structure of 1,3-bis(2-cyanophenyl) triazene (Fig. 1) based on a single-crystal X-ray structural analysis.

The compound L = 1,3-bis(2-cyanophenyl)triazene was prepared by the dropwise addition of 2.07 g (0.03 mol) of NaNO<sub>2</sub> in 20 ml of distilled water to a beaker containing 5.9 g (0.05 mol) of 2-aminobenzonitril and 6.48 ml (0.81 mol) of a HCl solution ( $d = 1.18$  g/ml) placed in a cold water bath. After 1/2 h stirring, CH<sub>3</sub>COONa·3H<sub>2</sub>O (13.6 g) in 20 ml of distilled water was added to the solution. The resulting yellow precipitate appeared after 15 min, evaporated to dryness in air, and was crystallized from diethyl ether in a freezer for three days. Large needle-like yellow crystals of the title compound formed under these conditions, and were isolated in 42% (2.59 g) yield; M. P., 127 - 129°C. Data for the structure determination were collected at 100 K, and the structure was solved using direct methods and refined on  $F^2$  by full-matrix least-squares using the program SHELXTL-2001.<sup>2</sup> Complete

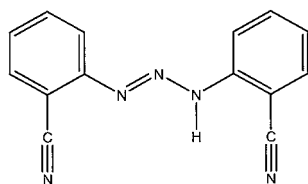


Fig. 1 Chemical structure of 1,3-bis(2-cyanophenyl)triazene.

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data-collection parameters and details of the structure solution and a refinement are given in Table 1. The hydrogen atoms attached to N atoms were found in a difference Fourier synthesis. All of the hydrogen atoms were included in the calculation using a riding atom model with  $U_{\text{iso}}(\text{H})$  parameters equal to  $1.2U_{\text{eq}}(\text{C}_i)$ ,  $1.2U_{\text{eq}}(\text{N}_i)$  where  $U(\text{C}_i)$  are equivalent thermal parameters of the carbon atoms, to which corresponding H atoms are bonded;  $U(\text{N}_i)$  are the equivalent thermal parameters of the corresponding nitrogen atom.

Crystallographic data show the presence of two kinds of the same molecule, defined as L and L', which are slightly different

Table 1 Crystal data and structure refinement details for L

Formula: C <sub>14</sub> H <sub>9</sub> N <sub>5</sub>	
Formula weight: 247.26	
Crystal system: triclinic	
Space group: $P\bar{1}$	$Z = 4$
$a = 6.818(3)\text{\AA}$	
$b = 7.642(3)(12)\text{\AA}$	
$c = 23.848(9)(11)\text{\AA}$	
$\alpha = 90.911(8)^\circ$	$\beta = 90.983(7)^\circ$
$\gamma = 105.970(7)^\circ$	
$V = 1194.3(8)\text{\AA}^3$	
$T = 100(2)\text{K}$	
$D_x = 1.375\text{ Mg m}^{-3}$	
No. of reflections = 2530	
$2\theta_{\text{max}} = 52$ with Mo $K_\alpha$	
$R1 = 0.0891$ , $wR2 = 0.1653$	
$(\Delta\sigma)_{\text{max}} < 0.001$	
$(\Delta\rho)_{\text{max}} = 0.350\text{ e}\text{\AA}^{-3}$	
$(\Delta\rho)_{\text{min}} = -0.271\text{ e}\text{\AA}^{-3}$	
Measurement = Bruker SMART APEX2 CCD area detector	
Program system = Bruker (2005). APEX2 software package,	
Bruker AXS Inc., 5465, East Cheryl Parkway, Madison, WI 5317.	
Structure determination = SHELXTL98	
Refinement: full-matrix least-squares on $F^2$	

CCDC 677843 contains the supplementary Crystallographic data for this paper. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

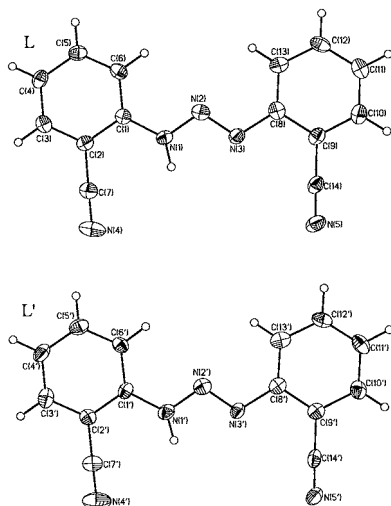


Fig. 2 ORTEP view of molecules of types L and L'.

Table 2 Bond lengths [Å] and angles [°] for L

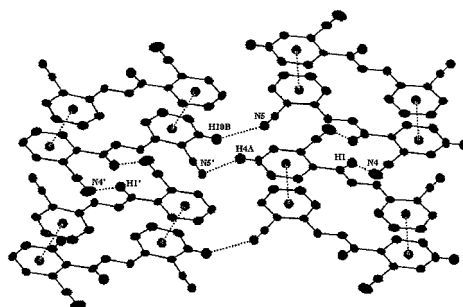
Atoms	Bonds & Angles	Atoms	Bonds & Angles
N(1)-N(2)	1.330(5)	N(1')-N(2')	1.335(5)
N(1)-C(1)	1.396(5)	N(1')-C(1')	1.391(5)
N(2)-N(3)	1.293(5)	N(2')-N(3')	1.289(5)
N(3)-C(8)	1.413(5)	N(3')-C(8')	1.423(5)
N(4)-C(7)	1.152(5)	N(4')-C(7')	1.157(6)
N(5)-C(14)	1.151(5)	N(5')-C(14')	1.145(6)
N(2)-N(1)-C(1)	117.9(3)	N(2')-N(1')-C(1')	117.5(4)
N(3)-N(2)-N(1)	111.0(3)	N(3')-N(2')-N(1')	110.3(4)
N(2)-N(3)-C(8)	113.4(3)	N(2')-N(3')-C(8')	113.8(4)
C(6)-C(1)-N(1)	123.1(4)	N(1')-C(1')-C(6')	123.5(4)
N(1)-C(1)-C(2)	117.9(4)	N(1')-C(1')-C(2')	117.8(4)
N(4)-C(7)-C(2)	178.9(5)	N(4')-C(7')-C(2')	179.4(6)
C(13)-C(8)-N(3)	125.6(4)	C(13')-C(8')-N(3')	125.0(4)
C(9)-C(8)-N(3)	114.4(4)	C(9')-C(8')-N(3')	114.9(4)
N(5)-C(14)-C(9)	177.4(5)	N(5')-C(14')-C(9')	178.0(5)

in bond distances and angles. An ORTEP diagram is shown in Fig. 2. The molecular structure of L confirms the expected *trans* stereochemistry about the N1=N2 double bond. A typical feature of free 1,3-diaryltriazenes is delocalization of the  $\pi$  electrons on the triazene group towards to the terminal aryl substituents. This behavior is supported by the deviations observed from the normal N-N and C<sub>Aryl</sub>-N bond lengths. The N1=N2 bond [1.330(5)Å] is longer than the characteristic value for a double bond (1.236 Å), whereas the N2-N3 bond [1.293(5)Å] is shorter than the characteristic value for a single bond (1.404 Å).<sup>3</sup> On the other hand, the N3-C8 [1.413(5)Å] and N1-C1 [1.396(5)Å] bonds are shorter than the characteristic N-C<sub>Aryl</sub> single bonds (secondary amines, R<sub>2</sub>NH, R = Csp<sup>2</sup>; 1.452 Å).<sup>4</sup> The important bond distances and angles are given in Table 2.

Table 3 Hydrogen bonds for L [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...N(4)#1	0.90	2.33	3.071(6)	140
N(1')-H(1')...N(4')#2	0.90	2.38	3.095(6)	136

Symmetry transformations used to generate equivalent atoms: #1  $-x+1, -y+1, -z$  #2  $-x+1, -y+2, -z-1$ .

Fig. 3 Crystal packing fragment along the *a* crystal axes. Hydrogen atoms are not depicted for clarity (●, centroid).

Two molecules of L form a dimer through intermolecular hydrogen bonds D-H...A1, A1' (D = donor atom, A = acceptor atom), N1-H1...N4, N1'-H1'...N4' (Table 3). These dimers polymerized through non-classical hydrogen bonds as well as  $\pi$ - $\pi$  stacking interactions. The already mentioned non-classical hydrogen bonds form as C-H...N (C10'...N5 = 3.409 Å, C10'-H10B...N5 = 150.44° (*x, y, z*); C10...N5' = 3.515 Å, C10-H10A...N5' = 145.28° (*x, -1+y, z*)).

The parallel directions of aromatic rings indicate the presence of strong face to face  $\pi$ - $\pi$  stacking interactions. The shortest distances for L are C3...C10 (3.354(6)Å), C1...C8 (3.408(6)Å) and the interplanar distance is 3.362(4)Å ( $1-x, -y, -z$ ). The shortest distances for L' are C3'...C10' (3.364(6)Å), C1'...C8' (3.399(6)Å) and the interplanar distance is 3.386(9)Å ( $1-x, 1-y, 1-z$ ) (Fig. 3). These interactions extend the two-dimensional chain further into a three-dimensional network.

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