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Journal of Molecular Structure 749 (2005) 60–69

Journal of MOLECULAR STRUCTURE

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Transformation of one of two C≡N groups of *o*-dicyanobenzene in the presence of cyanoguanidine. Crystal and gas-phase structure of 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine

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Received 7 June 2004; revised 25 August 2004; accepted 1 September 2004

Abstract

The transformation of one C≡N group in *o*-dicyanobenzene in the presence of cyanoguanidine yielding the melaminium derivative in crystalline form has been performed. In the final step of the closing of 1,3,5-triazined ring both hydrogen atoms of one amine group in cyanoguanidine should be transferred to the C≡N group. Additionally, it has been stated that due to the steric effect of the triazine ring formed from cyanoguanidine and one of cyano group of *o*-dicyanobenzene, the transformation process of the second C≡N group in *o*-dicyanobenzene in the presence of excess of cyanoguanidine is impossible. The 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine crystallises in the centrosymmetric space group of triclinic system. In the crystal the 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine molecule is non-planar due to the steric effect of triazine and cyano groups. The interaction of polar C≡N group with the nitrogen atom of triazine ring makes the rotation of one ring in relation to other by 22.1° as shown by the ab initio full optimised molecular orbital calculation performed on isolated molecule that corresponds to the gas-phase geometry. In the crystal the rotation angle is almost two times greater due to the intermolecular interaction and hydrogen bonding system. The molecules related by the inversion center interact via two pairs of almost linear N–H⋯N hydrogen bonds forming chains. The chains via more bent N–H⋯N hydrogen bonds form two-dimensional layers parallel to the (110) plane. The hydrogen bonding system and π–π interactions between the rings are responsible for the arrangement of molecules in the crystal. The molecular orbital calculations and conformational analysis have shown four equivalent minima and two pairs of maximum on the potential energy surface. The highest rotational barrier is almost the half of the hydrogen bond energy.

Keywords: Triazine derivative; Transformation; Crystal structure; Ab initio calculation

1. Introduction

Our interest in the investigations of the cyanocompounds such as dicyanobenzene isomers [1–6], 2,3-dicyanonaphthalene [7], cyanopyridine isomers [8] and others [9] arise from their possibilities to catalytic oligomerization with the formation of phthalocyanines [10], naphthalocyanines [11] and other oligomers (dimers and trimers) [12–14]. Additionally, due to their donation feature they are useful in the field of coordination chemistry and in particular to complexation of metallophthalocyanines [15–17]. The catalytic oligomerization with the formation of the phthalocyaninato macroring from the *o*-dicyanobenzene molecules in the presence of the metal requires: (a) the transformation of both functional C≡N groups with concomitant change of the hybridisation of the orbitals on the C atoms from sp to sp^2 of both C≡N groups, and (b) incorporation of the electrons, released from the metal (which has been oxidised) to the common π-electron conjugated system (see Scheme 1).

In the course of our work on phthalocyanine synthesis, we have stated many times that prolonged heating of the *o*-dicyanobenzene with powdered metals leads not only to the metallophthalocyanines in crystalline form (the main product), but also leads to the formation a colourless crystals stable above the melting point of *o*-dicyanobenzene.

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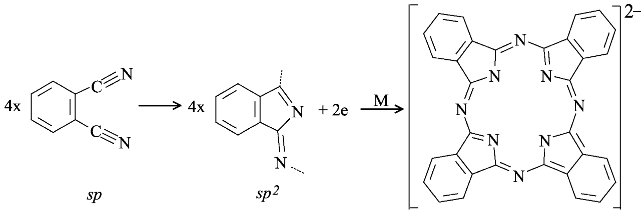
doi:10.1016/j.molstruc.2004.09.012

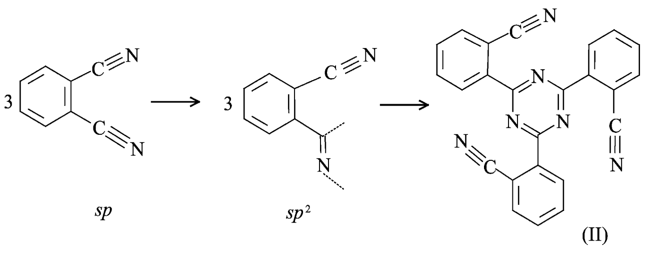


Scheme 1.

Investigations of these crystals have shown that during prolonged heating of *o*-dicyanobenzene the trimerization with the changing of hybridisation from sp to sp^2 on only one C≡N group takes place (see Scheme 2).

The trimer of *o*-dicyanobenzene belongs to the 1,3,5-triazine derivative—a very important class of organic compounds useful in the organic synthesis and technology. The basic compound of this class forms in the C≡N group transformation in the sequence: cyanamide → cyanoguanidine → melamine [18]. Investigations of substituted triazine derivatives have also focused on use as herbicides and pesticides in agriculture [19,20]. More recently, attention has also been focused on the use of triazine derivatives to form, by self-assembly of components that contain complementary arrays of hydrogen bonding sites, supramolecular networks via multiple hydrogen bonding system [21–24]. The developed well-defined supramolecular structures are promising to use as materials for non-linear optics [25] and semiconducting devices [26].

To expand the understanding of the functionality of the C≡N group, in this work we investigate the transformation of the C≡N group(s) in *o*-dicyanobenzene in the presence of cyanoguanidine, since it would also be interesting how the C≡N groups of *o*-dicyanobenzene would behave in the presence of the readily transformative C≡N group from another compound. Additionally, the X-ray structural investigations of the obtained compound in the crystalline form have been supported by the molecular orbital calculations. Comparison of the X-ray and gas-phase (ab initio) parameters and the calculated barriers along the interring C–C bond would be helpful to understand the nature of the intermolecular interactions present in the crystal, whereas the distribution of the charge density in the title molecule enables inside into the nature and character of the chemical bonds, and also indicate the active site(s) in the molecule in which the S_N or S_E reactions are possible.



Scheme 2.

2. Experimental

Preparation. Cyanoguanidine (99% purity) and *o*-dicyanobenzene (99.5% purity) were purchased from Sigma-Aldrich and used for the synthesis without purification. The cyanoguanidine was mixed with *o*-dicyanobenzene in the molar proportion of 1:1. Next the sample was pressed into pellets, and they were inserted into an evacuated glass ampoule and sealed. The ampoule (ca. 15 cm long) was annealed in the temperature gradient, hot zone—at about 220 °C, in which were the pellets, cool zone—at about 200 °C. After one day colourless single crystals were present in the ampoule. By crushing of the ampoule no enhanced pressure in it has been stated. An elemental analysis indicates on the composition of $C_{10}H_8N_6$ and the X-ray analysis gives the structure—2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine (found: C, 56.52; H, 3.82; N, 39.66%, calculated for $C_{10}H_8N_6$: C, 56.59; H, 3.80 and N, 39.61%), thus only one group of *o*-dicyanobenzene undergoes transformation. Therefore, the reaction of *o*-dicyanobenzene with cyanoguanidine has also been performed in the same reaction conditions as previously, but the reagents were taken in the molar proportion of 1:2. After one day in the ampoule two kinds of colourless crystals have been observed. However by a crushing, contrary to the first ampoule (the reagents taken in the molar proportion of 1:1) of the second ampoule (the reagents taken in the molar proportion of 1:2) an explosion and sharp smell have been stated. Selected single crystals were checked on a KUMA KM-4 CCD diffractometer. One kind of the crystals is identical with those obtained in the reaction of *o*-dicyanobenzene with cyanoguanidine taken in the molar proportion of 1:1, whereas the second kind of the crystals is known monoclinic form of melamine [27]. Always in the reaction of *o*-dicyanobenzene with the excess of cyanoguanidine in relation to *o*-dicyanobenzene (more than 1:1) the monoclinic melaminium crystals have been observed and have been checked several times using the different molar proportion of cyanoguanidine to *o*-dicyanobenzene (1.5:1, 2:1, 3:1, 4:1).

IR spectroscopy. IR spectrum (see Fig. 1) of solid material as a Nujol mulls was recorded at room temperature on a Bruker IFS 113 V FTIR spectrometer (4000–400 cm^{-1}). Resolution was set to 2 cm^{-1}. Most intense bands, ν_{max} (cm^{-1}): 3460, 3449 (ν_{as} NH_2), 3325 (ν_{sym} NH_2), 3160 (hydrogen bond N–H···N + side-chain asymmetric C–N stretching), 2228 (C≡N), 1637 (NH_2 bending), 1543 (ring quadrant stretching), 1255, 1208 (side-chain in plane C–N–C and N–C–N bending), 988 (triazine ring), 774 (ring-sextant out-of-plane bending), 557 (side-chain in plane N–C–N bending), 488 (contribution tone NH_2-bending + NH_2-rocking).

X-ray crystallography. A colourless single crystal of 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine with approximate dimensions of 0.28×0.22×0.20 mm was used for data collection on a four-circle KUMA KM-4

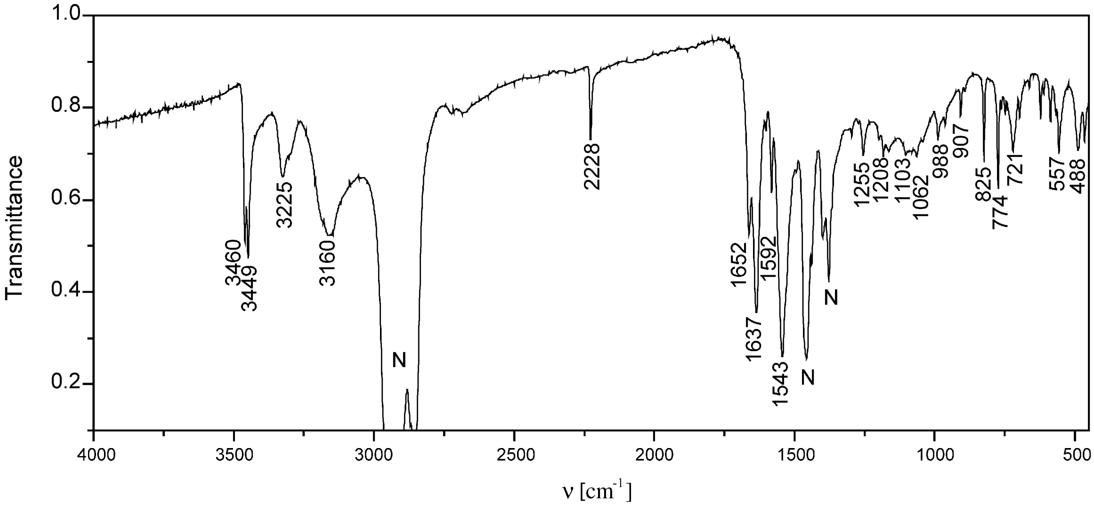


Fig. 1. IR-spectrum of 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine as Nujol mulls. The bands of the Nujol are assigned as N.

diffractometer equipped with a two-dimensional area CCD detector. The graphite monochromatised Mo Kα radiation ($\lambda = 0.71073$ Å) and ω-scan technique with $\Delta\omega = 0.75°$ for one image were used for data collection. The 960 images for six different runs covering over 99% of the Ewald sphere were performed. The lattice parameters were refined by least-squares methods on the basis of all collected reflections with $F^2 > 2\sigma(F^2)$. One image was monitored as a standard for every 60 images. Integration of intensities, correction for Lorenz and polarisation effects were performed using KUMA KM-4 CCD software [28]. The face-indexed analytical absorption was calculated using the SHELXTL program [29].

Table 1
Crystallographic data for 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine, details for data collection and refinement parameters

Formula	$C_{10}H_8N_6$
Mol. weight	212.22
Crystal system, space group	Triclinic, *P*-1
Unit cell dimensions *a*, *b*, *c* (Å)	7.281(1), 7.660(1), 9.466(2)
α, β, γ (°)	101.64(1), 103.80(1), 91.85(1)
Volume, *V* (Å^3)	500.36(14)
Z	2
D_{calc} (g/cm^3)	1.409
D_{obs} measured, flotation (g/cm^3)	1.40
Radiation, Mo Kα (Å)	$\lambda = 0.71073$
2θ range	3–56
Refls. collected	5925
Independent refls.	2401 ($R_{int} = 0.0195$)
Observed refls.	1491
Absorption coefficient, μ (mm^{-1})	0.095
Correction	Lorenz, polarisation, face-indexed analytical absorption, $T_{max.} = 0.9765$, $T_{min.} = 0.9662$
Refinement on F^2	
$R(F^2 > 2\sigma(F^2))$[a]	0.0351
wR (F^2 all reflections)[b]	0.0723
Goodness-of-fit, *S*	1.001
Residual electron density, e Å^{-3}	+0.186, −0.161

[a] $R = \sum ||F_o| - |F_c|| / \sum F_o$.

[b] $wR = \{\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.0297P)^2$, where $P = (F_o^2 + 2F_c^2)/3$.

The structure was solved by direct methods and refined with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXL-97 program [30]. The hydrogen atoms were located from difference Fourier maps, and their positional parameter were refined, but temperature factors were constrained with the $U_{iso} = 1.2U_{iso}$ of the carbon atoms joined directly the H atom, or $U_{iso} = 1.2U_{iso}$ of the nitrogen atoms joined directly the H atom. The final difference Fourier maps showed no peaks of chemical significance. The final agreement factors and details of data collection are summarised in Table 1. Final atomic coordinates and equivalent thermal displacement parameters are listed in Table 2.

Theoretical calculations. Ab initio molecular orbital calculations were performed with the GAUSSIAN98 program

Table 2
Final atomic coordinates and equivalent isotropic displacement parameter for 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine, $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i a_j \mathbf{a}_i \mathbf{a}_j$ (Å^2)

Atom	*x*	*y*	*z*	U_{eq}
C1	0.24629(15)	0.44673(14)	0.31640(12)	0.0322(3)
C2	0.28673(17)	0.27382(16)	0.26424(14)	0.0396(3)
C3	0.31947(18)	0.15443(17)	0.35751(17)	0.0475(4)
C4	0.31156(19)	0.20442(18)	0.50334(16)	0.0494(4)
C5	0.27275(17)	0.37544(17)	0.55866(15)	0.0426(3)
C6	0.24041(15)	0.49727(14)	0.46604(12)	0.0328(3)
C7	0.21314(16)	0.67673(17)	0.53532(13)	0.0367(3)
C8	0.20730(16)	0.57194(14)	0.21379(11)	0.0312(3)
C9	0.26598(17)	0.67798(15)	0.02214(12)	0.0364(3)
C10	0.04198(16)	0.79195(14)	0.13505(12)	0.0336(3)
N1	0.20253(16)	0.81451(14)	0.60520(12)	0.0505(3)
N2	0.30998(14)	0.56207(12)	0.11287(10)	0.0368(3)
N3	0.13322(14)	0.79450(12)	0.02765(10)	0.0370(3)
N4	0.07374(13)	0.68123(12)	0.23157(10)	0.0358(2)
N5	0.36473(17)	0.67691(16)	−0.08056(12)	0.0540(3)
N6	−0.09035(15)	0.90658(14)	0.14726(12)	0.0440(3)

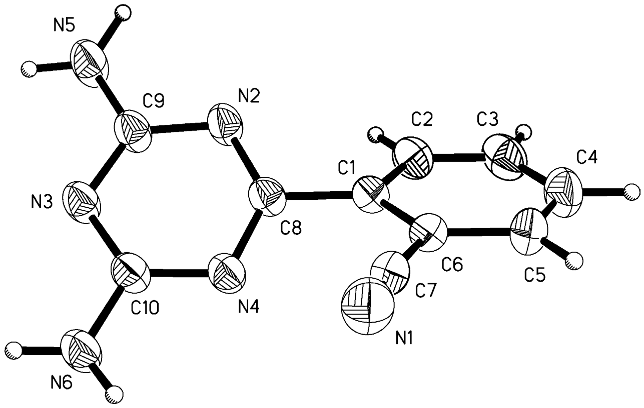


Fig. 2. View of the X-ray molecular structure of 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine with the atom labelling. Thermal ellipsoids are shown at a probability level of 50%. H atoms are shown as spheres with arbitrary radii.

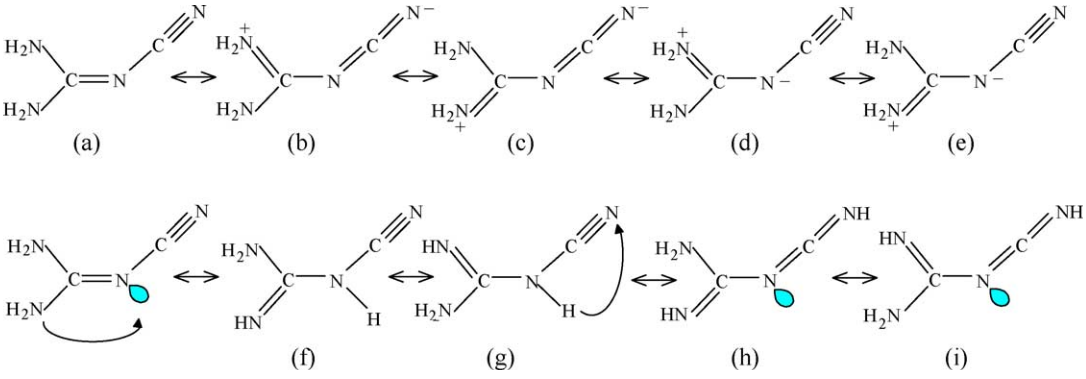
package [31] at the Hartree–Fock level of theory. Full geometry optimisation was performed with the 6-31G(d,p) basis set starting from the X-ray geometry. As convergence criterion the threshold limits of 0.00025 and 0.0012 a.u. were applied for the maximum force and the displacement, respectively. The rotation barriers of the 2-cyanophenyl and triazine rings around the inter-rings C–C bond were calculated using the same basis set functions and the GAUSSIAN98 program. In this case, all the full optimised parameters were kept frozen, while the ring of 2-cyanophenyl was rotated in steeps of 5° around the inter-rings C–C bond (C1–C8 bond, see Fig. 2). The highs of the rotation barriers were then derived from the variations of the total energy as functions of the rotation angle (the torsion angle of C2–C1–C8–N2 that define the inter-rings dihedral angle). The analysis of the theoretical charge density $\rho(r)$ and Laplacian $\nabla^2\rho(r)$ at the bond critical points were calculated using the AIMPAC program [32]. The topological properties of the charge density distribution are summarised in terms of their critical points, i.e. the points where $\nabla(\rho(r))$ is equal to zero.

3. Results and discussion

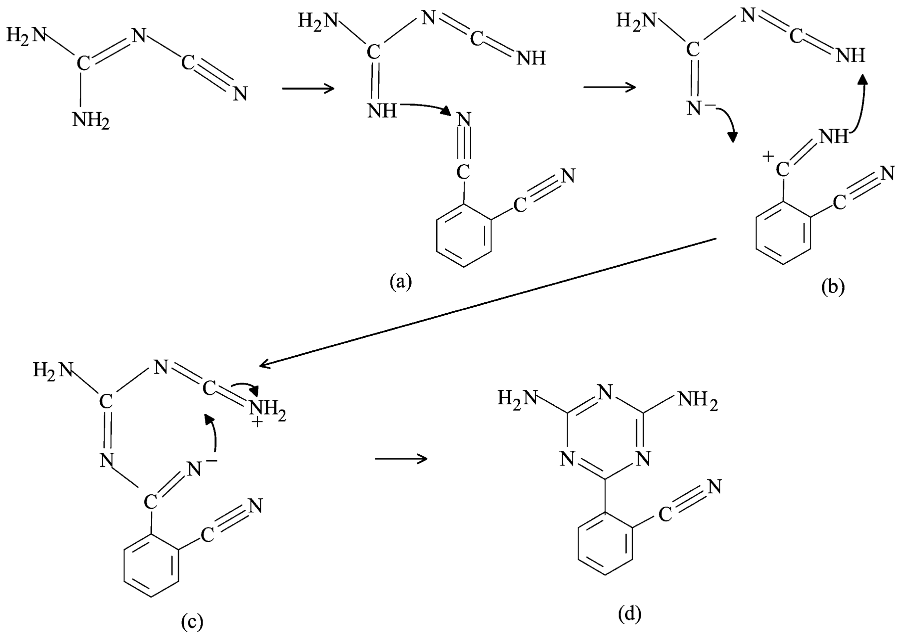
Synthesis. The transformation of only one of two C≡N groups in *o*-dicyanobenzene in the presence of cyanoguanidine takes place with the formation of triazine derivative. The X-ray determination of the charge density in cyanoguanidine [33] shows, that to explain the structure of cyanoguanidine molecule at least five resonance structures should be taken into account (Scheme 3, resonance structures of a–e).

The contribution of the respective canonical form in the real structure is significant, since the observed bond lengths [33] as well as the net atomic charges on the atoms of cyanoguanidine molecule are intermediate between the standard values [34]. The shortening of the C≡N bond explains well the (b)–(e) canonical forms. Besides these five resonance structures of cyanoguanidine molecule, few others canonical forms can be proposed (Scheme 3, resonance forms of h and i). The canonical forms with the imine group, that form as a result of H^+ migration from the amine group to the highly electronegative cyano group, will be helpful for understanding the reaction mechanism of cyanoguanidine with *o*-dicyanobenzene with the formation of 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine as illustrates Scheme 4.

The cyanoguanidine in the (h) or (i) canonical forms interacts with the C≡N group of *o*-dicyanobenzene (Scheme 4(a)). The N atom of cyano group of *o*-dicyanobenzene with the negative charge accepts the H^+ forming the imine group. This process yields the change of the hybridisation of the orbitals from sp to sp^2 for the C atom of the interacting CN group (4b). Next the terminal NH group of cyanoguanidine accepts the proton forming NH_2 group with the positive charge on the N atom. Simultaneously, the positively charged C atom interacts with negatively charged N atom forming C–N bond (4c). Consequently, the NH_2^+ group accepts one pair of electron from the C=N bond (4c), this process yields to the change of the hybridisation from sp to sp^2 of the orbitals of the C atom and finally the C–N bond closes the triazine ring (4d). Thus, in the process of triazine



Scheme 3.

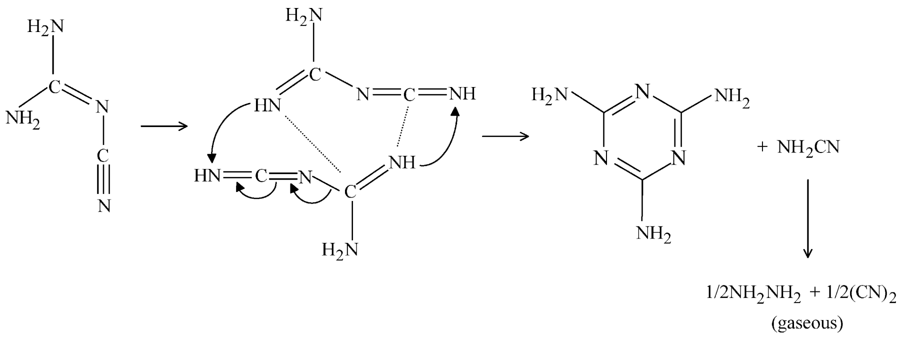


Scheme 4.

ring formation both H atoms of one amine group are transferred to the N atom of C≡N group of cyanoguanidine. The formation process of 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine from *o*-dicyanobenzene and cyanoguanidine takes place independent on the molar proportion of the substrates (1:1 as well as in the excess of cyanoguanidine). The transformation process of both C≡N groups of *o*-dicyanobenzene with the formation of two triazine rings is not possible (see experimental part, the reaction of *o*-dicyanobenzene with cyanoguanidine taken in the molar proportion of 1:2) due to the steric effect of the large diaminotriazine group joined in the *o*-position in relation to the CN group (4d). The excess of cyanoguanidine used under reaction conditions undergoes dimerization with the formation of melamine crystals and with partly decomposition according to Scheme 5.

The gaseous products and the formation of melamine crystals are in agreement with the observations and the results of the experiment. In the sample with molar proportion of 1:2, by crushing of the ampoule it was an explosion and sharp smell, melamine crystals have been identified on single crystal KUMA KM-4 diffractometer.

The IR spectrum of 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine (Fig. 1) shows the expected band of the C≡N group at ~2228 cm^{-1}, i.e. it is shifted by ~4 cm^{-1} to the lower frequency in relation to that observed in the spectrum of *o*-dicyanobenzene (2232 cm^{-1}), since the N atom of the C≡N group is involved in the hydrogen bond. This C≡N···H hydrogen bonding interaction results in the decrease of the population for molecular orbital of C≡N group, hence decrease in bond order and the stretching force constant yielding to the shift of the absorption band. The bands at 3460 and 3449 cm^{-1} can be attributed to the NH_2 asymmetric stretching vibrations of the two NH_2 groups of triazine and the broad band at ~3325 cm^{-1} is attributed to the NH_2 symmetric stretching vibration. The broad band at ~3160 cm^{-1} supported by the analysis of the IR-spectrum of melamine [35] can be assigned to a mode having a contribution of N–H···N hydrogen bond and side-chain asymmetric C–N stretching. In the spectral region of



Scheme 5.

1650–1500 cm^{-1} two strong bands at 1637 and 1543 cm^{-1} and one weaker at ~1592 cm^{-1} are observed. According to the literature, the first can be attributed to NH_2-bending, while the second can be assigned to the ring-quadrant stretching [36]. The other bands at 1255 and 1208 cm^{-1} can be attributed to side-chain in plane C–N–C and N–C–N bending [36,37]. The weak band at 988 cm^{-1} originates from triazine ring N in-phase radial type of vibration [37]. The band at 774 cm^{-1} can be assigned to ring-sextant out-of-plane bending, the band at 557 cm^{-1} to the side-chain in plane N–C–N bending and the band at 488 cm^{-1} to the contribution tone of NH_2-bending and NH_2-rocking vibration [36,37]. The bands of the C–H of the phenyl ring are overlapped with the bands of the Nujol (1377, 1458, 2854 and a broad band at 2923 cm^{-1}).

X-ray and gas-phase structure. The molecular geometry of the 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine obtained by the single crystal X-ray analysis with the atomic labelling is shown in Fig. 2. The X-ray experimental geometrical parameters are collected in Table 3, which also comprises the ab initio fully optimised parameters that correspond to the gas-phase. The absolute energy calculated using the HF/6-31G(d,p) basis set functions was found to be −710.117 Hartree and is a global minimum on the potential energy surface and the calculated dipole moment of the 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine molecule is 4.17 D.

Both aromatic six-membered rings, i.e. benzene and triazine, in the crystal are planar (the distortions of the C atoms are smaller than 0.003(1) and 0.005(1) Å in benzene and triazine rings, respectively), but show, especially the triazine ring, noticeable distortions from the ideal hexagonal shape. The internal C–N–C angles in the triazine ring are significantly smaller than 120° while the internal N–C–N angles are significantly greater than 120°. This is a result of the steric effect of a lone-pair of electrons at the N atoms of triazine rings, predicted by the valence-shell electron-pair repulsion theory (VSEPR) [38,39]. The ab initio optimised geometry of the triazine ring shows a similar correlation between the internal C–N–C and N–C–N angles within the ring as observed in the crystal. Thus, the triazine ring distortion mainly results from the steric effect on lone-pair of electron, while the intermolecular interactions and crystal packing forces play a smaller role. The differences between the C–C bonds and C–C–C angles in the 2-cyanophenyl ring arise mainly from the substitution effect of the polar C≡N group and diaminotriazine ring. The C–CN distance of 1.441(2) is slightly longer and the triple C≡N bond is slightly longer than found in the crystal of *o*-dicyanobenzene, whereas the C–C≡N angle of 172.1(1)° is significantly distorted from the almost linear form (179.5(2)°) observed in the crystal of *o*-dicyanobenzene [1]. The optimised molecule in the gas-phase shows quite similar distortion of the C–C≡N angle (172.8°) as found in crystal. This is likely due to steric effect of relatively great diaminotriazine group substituted in the *o*-position and the repulsion interaction between the polar C≡N group and the N atom of the triazine ring that contains lone-pair of electrons. This interaction makes the rotation of the rings to each other around the inter-ring C–C bond. The rotation of the rings are observed in the crystal as well as in the gas-phase, but in the crystal the rotation of the rings is greater (dihedral angle between the rings equals to 37.22(5)) than in the gas-phase (22.1°) due to the hydrogen bonding systems, intermolecular interactions and the crystal packing forces.

Table 3
Bond distances and angles (in Å and °)

	X-ray	Gas-phase
C1–C2	1.3840(15)	1.389
C1–C8	1.4852(15)	1.493
C3–C4	1.3717(18)	1.383
C5–C6	1.3931(15)	1.391
C7–N1	1.1425(14)	1.136
C8–N2	1.3388(13)	1.320
C9–N3	1.3397(13)	1.324
C10–N6	1.3339(14)	1.336
C10–N4	1.3536(13)	1.335
C2–C1–C6	118.22(10)	118.4
C2–C1–C8	119.90(10)	118.5
C6–C1–C8	121.87(10)	123.1
C3–C2–C1	120.64(12)	121.3
C4–C3–C2	120.77(13)	120.1
C3–C4–C5	119.97(13)	119.6
C4–C5–C6	119.82(12)	120.6
C5–C6–C1	120.58(11)	120.1
C5–C6–C7	116.20(11)	115.2
C1–C6–C7	123.12(10)	124.7
N1–C7–C6	172.17(12)	172.8
N4–C8–N2	126.83(10)	125.8
N4–C8–C1	116.32(10)	117.2
N2–C8–C1	116.85(10)	117.0
N5–C9–N3	117.64(11)	117.4
N5–C9–N2	117.05(11)	117.0
N3–C9–N2	125.31(11)	125.6
N6–C10–N3	117.63(10)	118.2
N6–C10–N4	117.49(11)	116.7
N3–C10–N4	124.89(10)	125.1
C8–N2–C9	113.81(10)	114.3
C9–N3–C10	114.84(10)	114.3
C8–N4–C10	114.31(10)	114.9
C1–C6	1.4024(14)	1.401
C2–C3	1.3828(16)	1.383
C4–C5	1.3740(17)	1.382
C6–C7	1.4405(16)	1.449
C8–N4	1.3224(13)	1.310
C9–N5	1.3390(15)	1.339
C9–N2	1.3503(13)	1.333
C10–N3	1.3434(13)	1.323

Intermolecular interactions and the crystal packing. The molecules related by the inversion center interact via two pairs of almost linear N–H···N hydrogen bonds (Table 4) forming one-dimensional chains (Fig. 3). In the chains the triazine rings are coplanar, while the 2-cyanophenl rings are deviated from this plane. The complementary joined via N–H···N hydrogen bonds chains interact via more bent and weaker N–H···N hydrogen bonds between the amine

Table 4
Hydrogen-bonding geometry (Å, °)

D–H···A	D–H	H···A	D···A	D–H··· A
N5–H51···N2^{i}	0.97(2)	2.11(2)	3.075(2)	174(1)
N5–H52···N1^{ii}	0.91(2)	2.48(2)	3.320(2)	154(1)
N6–H61···N1^{iii}	0.90(2)	2.44(2)	3.119(2)	132(1)
N6–H62···N3^{iv}	0.92(2)	2.15(2)	3.068(2)	180(1)

Symmetry code: (i) $1-x$, $1-y$, $-z$, (ii) x, y, $z-1$, (iii) $-x$, $2-y$, $1-z$, (iv) $-x$, $2-y$, $-z$.

groups (as donor H) and cyano groups (as acceptor H) forming a two-dimensional sheets (Fig. 4) that in the crystal are located almost parallel to the (110) plane (Fig. 5). In one sheet the 2-cyanophenyl rings are located anti-parallel, so the interaction of polar C≡N groups is weak, and separated by ~3.52 Å. This value indicates π–π interactions between the phenyl rings, since this distance is comparable to the van der Waals distance between the aromatic ring system [40]. Thus, each 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine molecule in the crystal is involved into eight hydrogen bonds, in four of them as a donor H and in the remaining as an acceptor. One N atom of three of the triazine rings (N4) does not form any hydrogen bond, while the other two (N2 and N3) as acceptors form the almost linear hydrogen bonds that interconnect the molecules into chains. The N atom of cyano group is acceptor of two hydrogen bonds that interconnect the complementary N–H···N bonded chains (Fig. 3) into a two-dimensional layer (Fig. 4). These layers in the crystal are parallel to each other and parallel to the (110) plane (Fig. 5). There is no observed any hydrogen bonds between the layers, but the π–π interaction between the parallel benzene rings is possible, since these rings of

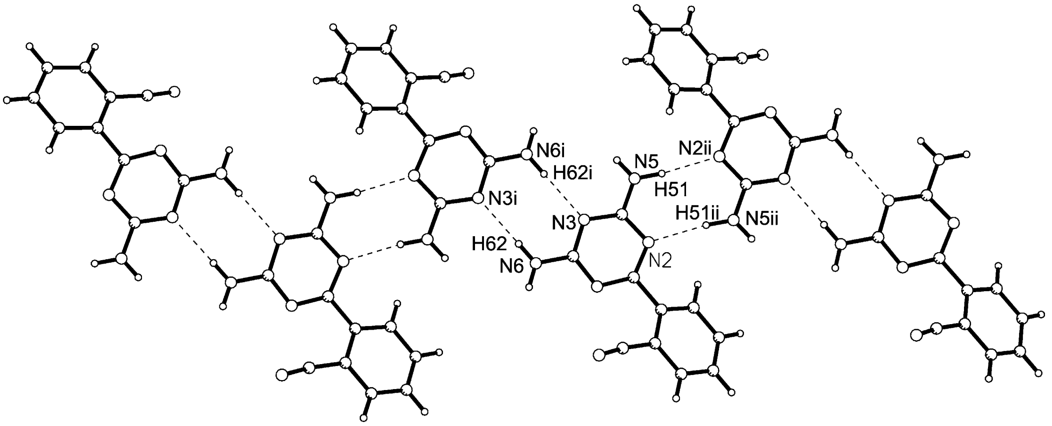


Fig. 3. Pseudo one-dimensional chain of the hydrogen bonded 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine molecules.

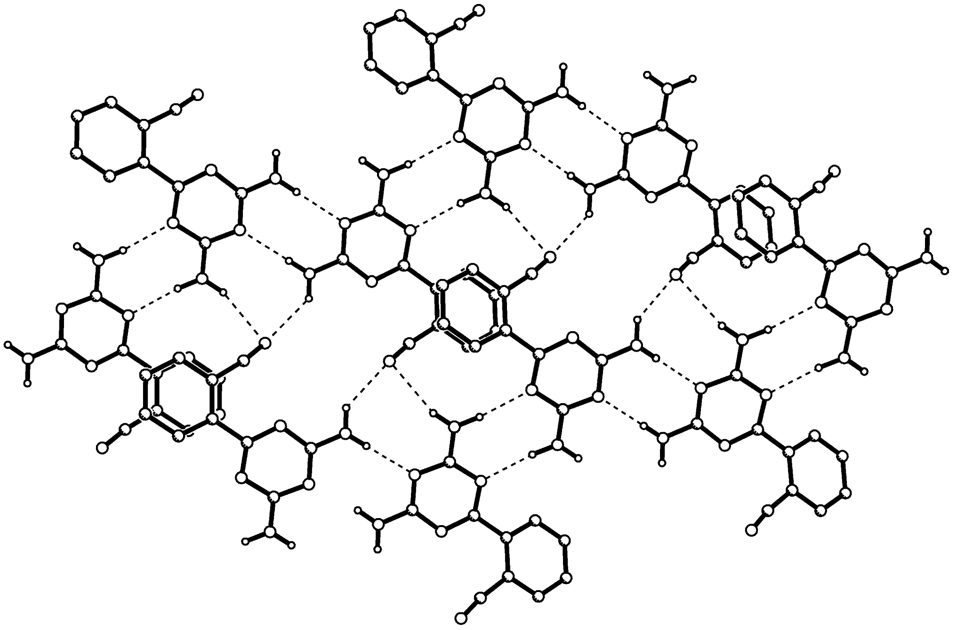


Fig. 4. Two-dimensional layer consists of interconnected two neighbouring chains of 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine showing the π–π interactions between the overlapped phenyl rings.

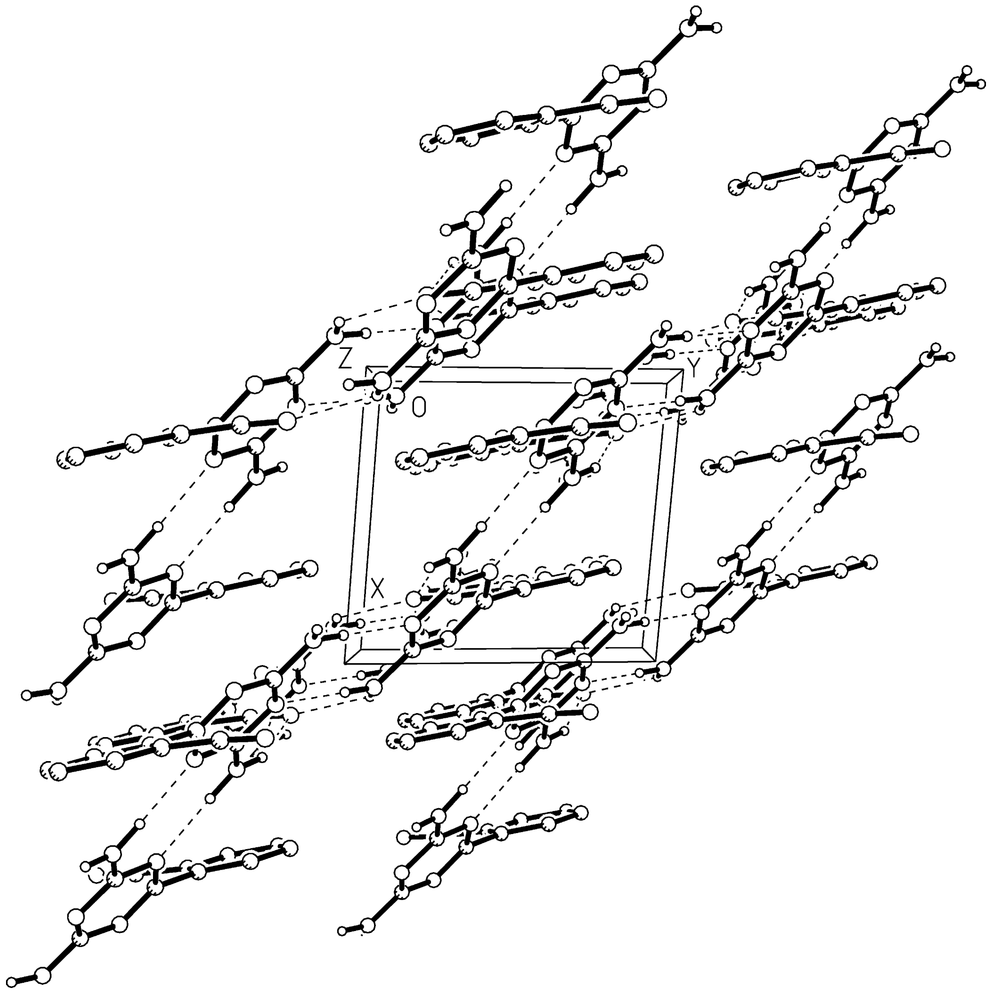


Fig. 5. View of the crystal packing showing the three neighbouring layers that are almost parallel to (110) plane. Dashed lines represent N–H···N hydrogen bonds.

neighbouring layers are separated by ~3.62 Å, while the triazine rings are separated by 3.66 Å. This kind of intermolecular interactions, i.e. anti-parallel orientation of polar cyano groups of 2-cyanophenyl rings, hydrogen bonding system, π–π interactions, gives rise to the relatively great crystal density ($d \sim 1.409$ g/cm^3).

Molecular conformation and rotational barriers. The rotation of one ring relative to the other around the inter-ring C–C bond in the crystal of title compound is hindered due to the intermolecular interactions that lead to the formation of N–H···N hydrogen bonding system as well as by the van der Waals interactions and the crystal packing forces. In the gas-phase, the rotation of the rings around the inter-ring C–C bond is possible. Molecular orbital calculations with full geometry optimisation performed on the isolated 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine molecule show similar non-planar conformation as in the crystal, however in the crystal due to the intermolecular interaction, the inter-planar angle (between the rings) is greater (37.2(1)°) than in the gas-phase (21.1°). The calculations located four equivalent minima and two pairs of equivalent maxima on the potential energy surface. The values of the rotation barriers were derived from the variation of the total energy as a function of the rotation angle of C2–C1–C8–N2 (this torsion angle define the dihedral angle between the rings) and the results are illustrated in Fig. 6. As can be seen from Fig. 6 during rotation of one ring relative to other from 0 to 360° four equivalent global minima of energy (at 21.1, 158.9, 201.1 and 338.9° or 0 ± 21.1° and 180 ± 21.1°) and two pairs of maximum energy (equivalent at 0 and 180° and at 90 and 270°) are observed. The lower barrier is observed at the angle of 0 and 180° and the higher barrier at 90 and 270°. The energy barrier at 0° (or equivalent at 180°) equals to ~2.1 kJ/mol. This relatively low barrier energy is due to delocalisation of the π electrons between the rings and the repulsion interaction between the polar C≡N group and the lone-pair of electron of the N atom of triazine ring. This interaction leads to the distortion of the C–C≡N angle from the linear form. The higher barrier energy of ~17.75 kJ/mol is found for the rotation angle of 90° (or equivalent at 270°). In this conformation the triazine and benzene rings are perpendicular to each other. This energy barrier is nearly half

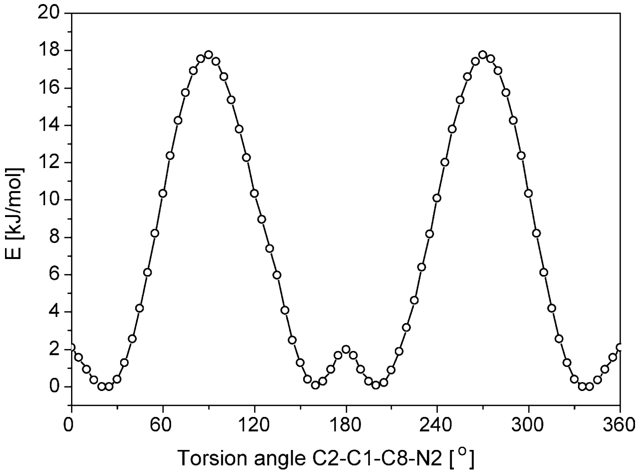


Fig. 6. Potential energy surface showing the rotational barriers during rotation of one ring in relation to other around the inter-ring C1–C8 bond computed by a molecular orbital calculations at the HF/6-31G(d,p) level.

of the hydrogen bond energy [37]. The 17.75 kJ/mol difference between the energy of the conformations of the molecule at 21.1 and 90° can be assigned to the sum of interaction energy between the polar CN group and lone-pair of electrons at the N atom of triazine ring and the π-delocalisation energy of the π-electrons that are slightly delocalised between the rings along the inter-ring C–C bond. At the rotation angle of 90°, the delocalisation of the π-electrons between the rings along the inter-ring C–C bond is impossible because of the symmetry of the orbitals. The lengthening of the inter-ring C1–C8 bond from 1.493 Å (at the rotation angle of 21.1°) to 1.511 Å (at 90°) supports this hypothesis. The value of inter-ring C1–C8 bond length has been obtained by molecular orbital calculations in which the torsion angle of C2–C1–C8–N2 was kept to 90° (the rings are perpendicular to each other). In the molecule with the lower energy two effects, i.e. repulsion interactions between the polar CN group with the lone-pair of electron on the N atom of triazine ring and the delocalisation of the π electrons between the rings along the C1–C8 play important role. Thus the inter-ring C1–C8 bond possesses a slight double-bond character as a result of delocalisation of the π electrons between the rings. This observation is quite similar to that found in 2-(3-pyridyl)-1,3,5-triazanaphthalene compound studied by us [14]. The contribution of the π electrons in the delocalisation between the rings clearly evidenced the ellipticity, ε [41]. The bond critical points are the 'staddle' points in the electron density along the bond between the joined atoms. At these staddle points (where $\nabla\rho=0$), the three principal curvatures have one positive value and two negative values defines the $(3,-1)$ bond critical points. The positive curvature (λ_3) being directly along the bond (bond path) and the negative (λ_1 and λ_2) perpendicular to the bond path define the interatomic surface between the bonded atoms. The value of the charge density (ρ) at the bond critical point indicates the bond order, while the two negative curvatures define the bond ellipticity, $\varepsilon=\lambda_1/\lambda_2-1$. Thus the ellipticity is a measure of the π-character of the bond, while the location of the bond critical points correlate to the polar character of the bonds [42]. The values of the charge density (ρ) at the bond critical points correlate with the bond order as well as with strength of the bonds [43]. The calculated bond ellipticity at the bond critical point of C1–C8 bond equals to 0.091 (for a typical single bond the value of ellipticity equals to 0). For a comparison, the calculated ellipticity for the aromatic C–C bonds of the 2-cyanophenyl ring in which the delocalisation of the π electron takes place ranges from 0.202 to 0.215 (see Table 5). The slightly differences of ε between the C–C bonds within the phenyl ring result from the substitution effect of CN group and diaminotriazine ring substituted to the phenyl ring, that slightly perturb the symmetric delocalisation of the π electrons present in the non-substituted benzene molecule.

Table 5
Charge density topological parameters calculated using HF/6-31G(d,p)

Bond	Length	ρ (e Å^{-3})	$\nabla^2\rho$ (e Å^{-5})	λ_1	λ_2	λ_3	ε	AT1-CP	CP-AT2
C1–C2	1.389	2.198	−24.271	−16.92	−13.91	6.56	0.211	0.710	0.680
C2–C3	1.383	2.216	−24.765	−17.11	−14.17	6.52	0.207	0.693	0.694
C3–C4	1.383	2.216	−24.765	−17.11	−14.17	6.52	0.207	0.694	0.693
C4–C5	1.382	2.221	−24.877	−17.20	−14.15	6.47	0.215	0.691	0.692
C5–C6	1.391	2.186	−24.045	−16.91	−13.66	6.53	0.206	0.675	0.717
C6–C1	1.401	2.141	−22.991	−16.43	−13.36	6.72	0.202	0.716	0.687
C1–C8	1.493	1.902	−20.145	−14.39	−13.31	7.58	0.081	0.734	0.759
N1–C7	1.136	3.302	17.198	−25.37	−24.89	67.45	0.019	0.721	0.415
N2–C8	1.320	2.489	−26.897	−21.34	−19.16	14.61	0.114	0.816	0.505
N2–C9	1.333	2.481	−26.130	−21.42	−19.15	14.45	0.119	0.812	0.523
N3–C9	1.324	2.487	−27.471	−21.93	−19.76	14.22	0.110	0.807	0.518
N3–C10	1.323	2.486	−27.192	−21.96	−19.47	14.24	0.128	0.811	0.515
N4–C8	1.310	2.529	−26.157	−21.97	−20.06	14.87	0.095	0.803	0.511
N4–C10	1.323	2.487	−27.188	−21.95	−19.46	14.22	0.128	0.809	0.516
N5–C9	1.339	2.122	−24.125	−20.67	−19.55	16.10	0.057	0.819	0.521
N6–C10	1.336	2.143	−24.329	−20.98	−19.73	16.37	0.063	0.816	0.522

The energy barrier at the 0° (or equivalent at 180°) of $\sim$2.1 kJ/mol is smaller than the *RT* value of $\sim$2.5 kJ/mol (at room temperature). Thus in absence of any specific interactions (as present in the crystal), the oscillation between the two global minima around the 0° (+21.1 and −21.1°) is possible at room temperature. Whereas the energy barrier at 90° (or equivalent barrier at 270°) is greater by a factor of $\sim$7 in relation to *RT* energy and the change of the conformation from 21.1° to the 158.9 is hindered at room temperature.

4. Conclusions

Only one C≡N group in *o*-dicyanobenzene undergoes transformation in the presence of cyanoguanidine yielding 2-(2′-cyanophenyl)-4,6-diamino-1,3,5-triazine in crystalline form. The interaction of the polar C≡N group with the nitrogen atom of triazine ring makes the rotation of one ring in relation to other by 22.1° as shown in the ab initio calculation. The steric effect of the formed diaminotriazine ring from the cyanoguanidine prevents the transformation of the second C≡N group that is located in the *o*-position in relation to the inter ring C–C bond. A question "How the transformation process of the C≡N group in the remaining two dicyanobenzene isomers (m-, and p-isomer) in the presence of cyanoguanidine take place?" is still open and is a subject of our work in the future.

5. Supplementary material

Additional material comprising full details of the X-ray data collection and final refinement parameters including anisotropic thermal parameters and full list of the bond lengths and angles have been deposited with the Cambridge Crystallographic Data Center in the CIF format as supplementary publication No. CCDC 240726. Copies of the data can be obtained free of charge on the application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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