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Tris(2-cyanophenyl)-1,3,5-triazine: a By-product of Metallophthalocyanine Synthesis

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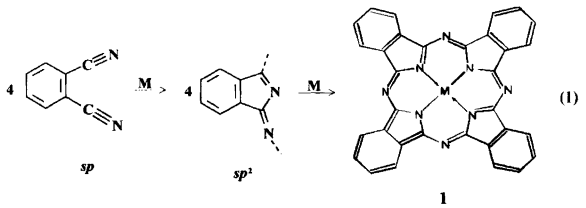
Tris(2-cyanophenyl)-1,3,5-triazine $\{[C_6H_4(CN)]_3C_3N_3\}$ has been identified as a by-product of the synthesis of metallophthalocyanines by IR and Raman spectroscopy and X-ray diffraction. Tris(2-cyanophenyl)-1,3,5-triazine in the solid state exists in two crystalline modifications: monoclinic – low temperature phase I, and triclinic – high temperature phase II. The monoclinic phase is stable up to 270 °C, while the triclinic phase is stable above this temperature. The molecular structures of tris(2-cyanophenyl)-1,3,5-triazine were determined by X-ray structure analysis. The experimental geometries of the molecule in both modifications are compared with *ab-initio* calculations. Some remarks related with the phase transition and the molecular architecture are given.

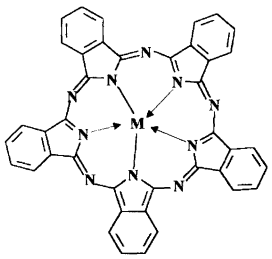
The oligomerization of the *o*-dicyanobenzene[1] in the presence of metals leads to the formation of phthalocyanine.[2,3] The metal present in the cyclotetramerization reaction of *o*-dicyanobenzene is usually coordinated by the formed four-dentate phthalocyaninato ligand, which leads to the formation of metallophthalocyanines.[4] The phthalocyanine consists of the four isoindole moieties linked together by four N-aza atoms. The formation of the phthalocyaninato macrocyclic ring from the *o*-dicyanobenzene molecules requires: (a) the transformation of both functional cyano groups with concomitant change of the hybridization of the carbon atoms from sp to sp^2 and (b) incorporation of the electrons, released from the metal which has been oxidized, to the common π electron conjugated system [eqn. (1)].



Scheme 1.

Depending on the reaction conditions and the nature of the metal used for the oligomerization of *o*-dicyanobenzene, several metallophthalocyanines may be formed: (a) normal phthalocyanines (monophthalocyanines, sandwich-type diphthalocyanines and triple-decker phthalocyanines) with four isoindole moieties (**1**),[5–14] (b) superphthalocyanines with five isoindole moieties (**2**),[15–17] (c) subphthalocyanines with the three isoindole moieties (**3**)[18–23] and (d) bicyclic phthalocyanines with six isoindole moieties in the macrocyclic ring (**4**).[24–27]

The common feature of these phthalocyanine macromolecules is a very strong absorption of light in the visible spectral range. Normal phthalocyanines (**1**) with a 18π electron system show a Q band at around 670 nm, regardless of the nature of the metal coordinated by the



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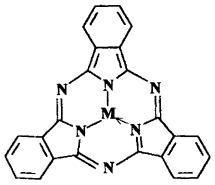

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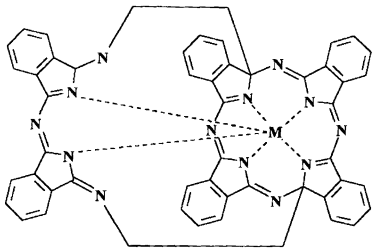

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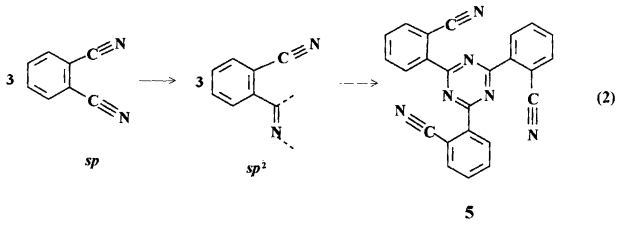

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Scheme 2.

chelate phthalocyaninato ligand. Superphthalocyanines (**2**) with a 22π electron system show a Q band at around 915 nm and are easily converted into phthalocyanines by reaction with metal chloride.[15] Subphthalocyanines (**3**) with the 14π electron system show a Q band at around 570 nm and are also converted into phthalocyanines by reaction with the 1,3-isoindolinediimine.[28,29] Although the number of the π electrons in the superphthalocyanine and subphthalocyanine rings is in agreement with the Hückel rule, all known super- and sub-phthalocyanines are non-planar, because the strain in these rings leads to the deviation from planarity. Bicyclic phthalocyanines with a 24π electron system show a Q band at around 720 nm.[30] Bicyclic phthalocyanines are also non-planar, because delocalization of the π electron system is interrupted by the two binder head C (sp^3) atoms, which link together the phthalocyaninato moieties in a bicyclic ring (**4**).[24–27]

During the course of our work on phthalocyanine synthesis[4,31] we have stated many times that prolonged heating of the starting mixture of *o*-dicyanobenzene with powdered metal leads not only to the metallophthalocyanine in crystalline forms – the main product, but may also lead to a colourless and transparent crystalline by-product, stable well above the melting point of the *o*-dicyanobenzene. Commercially available metallophthalocyanines are also often not chemically pure; they may contain different kinds and percentages of by-products. Often there is the unreacted *o*-dicyanobenzene or other substrate used in the synthesis, or metal-free phthalocyanine. For instance commercially available iron phthalocyanine may contain up to 30% metal-free phthalocyanine.[32] Therefore, in our studies we also pay attention to investigations of the by-products formed during the synthesis of the metallophthalocyanines.

During our studies on a series of metallophthalocyanines from *o*-dicyanobenzene and powdered metal (or intermetallic alloy) we have found that, under the specific conditions of the reaction, only one of the cyano groups of the *o*-dicyanobenzene undergoes transformation with the change of the hybridization of the carbon atom from sp to sp^2, which gives rise to the formation of the trimer of *o*-dicyanobenzene [eqn. (2)].

The trimer of *o*-dicyanobenzene is a derivative of 1,3,5-triazine – a very important class of compound useful in organic technology. Many substituted triazine compounds are used as herbicides and pesticides in agriculture.[33–37] The tris(2-cyanophenyl)-1,3,5-triazine (**5**) belongs to the family of 2,4,6-substituted triazines which are promising as materials for non-linear optics,[38] and semiconducting materials.[39] Several substituted 1,3,5-triazine compounds have been widely studied to expand the understanding of the physical-organic chemistry of the solid state, especially the investigation of the intermolecular hydrogen bonds, their nature and energies.[40–44] Moreover, we also found that the trimer of *o*-dicyanobenzene (**5**) crystallizes depending on the conditions in the two modifications – monoclinic (longitudinal form of the crystals) and triclinic (almost cubical form of the crystals). Additionally we found that the monoclinic form is stable below 270 °C; at higher temperature the monoclinic crystals are transformed into the triclinic modification, which is stable up to about 320 °C.

In this work we present the determination of the both crystal structure modifications and some features of the tris(2-cyanophenyl)-1,3,5-triazine (**5**) regarding the phase transition.

Experimental

Preparation. Tris(2-cyanophenyl)-1,3,5-triazine has been obtained[4] many times as a by-product during synthesis various metallophthalocyanines, but good quality crystals have now been obtained during the synthesis of magnesium phthalocyanine, which was studied by us as a model compound for a reversible binding of N_2 and O_2 molecules.[45] 1,2-Dicyanobenzene was mixed with the pure powdered magnesium in a molar proportion of 4 : 1 (with about 15% excess of 1,2-dicyanobenzene in relation to Mg). The mixture was pressed into pellets and the pellets were placed in an evacuated glass ampoule and sealed. The ampoule was heated at 210 °C for one day. At this temperature the 1,2-dicyanobenzene undergoes catalytic tetramerization forming the phthalocyanine units. Since after one day a considerable part of magnesium remained unreacted with the 1,2-dicyanobenzene with the formation of Mg-phthalocyanine, the temperature was increased to about 230 °C and the heating process was continued for about 20 h. At this temperature in addition to the magnesium phthalocyanine, colourless, transparent and longitudinal-shaped crystals were obtained as a stable by-product. Preliminary examination of the crystal by rotation and Weissenberg photographs indicated the monoclinic system. Anal. Found: C, 75.1;

N, 21.82; H, 3.08%. Calc. for $C_{24}H_{12}N_6$: C, 74.99; N, 21.86; H, 3.15%.

These monoclinic crystals were stable up to ≈270 °C. At this temperature the long transparent crystals underwent transformation into other crystals of almost regular cubic shape, which are stable up to about 325 °C (melting point). Rotation and Weissenberg photographs of these indicated a triclinic system. Elemental analysis gave the same results as for the crystals of the monoclinic system.

IR spectroscopy. IR spectra of the solid material (KBr discs) were recorded at room temperature on a Bruker IFS 113 V FTIR spectrometer (4000–600 cm^{-1}). Resolution was set to 2 cm^{-1}.

Raman spectroscopy. The Raman spectra were recorded at room temperature on a Bruker IFS-88 with FRA-106 attachment, Nd-YAG diode pump laser, $\lambda = 1.06$ μm, power 150 mW. Resolution was set to 2 cm^{-1}.

X-ray data collection. Both crystals were used for data collection on a four-circle KUMA KM-4 diffractometer equipped with a graphite monochromator. The unit cells were determined by a least-squares method on a fit of 25 reflections. A total of 6551 and 5321 reflections for monoclinic and triclinic crystals, respectively, were measured using the ω–2θ scan technique. Two standard reflections were monitored every 50 reflections. The intensity variations were 2.8 and 1.4% for the monoclinic and triclinic crystal, respectively. Intensities and their standard deviations were corrected for Lorenz and polarization effects. 3202 and 5321 independent reflections for the monoclinic and triclinic crystals, respectively, were used for structure solution and refinement.

Structure solution and refinement. Both crystal structures, especially the triclinic modification, proved extremely difficult to solve. Since (1) the molecule of tris(2-cyanophenyl)-1,3,5-triazine is non-centrosymmetrical and (2) $Z = 3$ for the triclinic crystal, the space group of the triclinic crystal is therefore $P1$. The structures were solved using SHELXS,[46] but only with TREF = 2000 and with the best E maps. For the monoclinic crystal direct methods gave the location of the 1,3,5-triazine ring and some C-atoms of the three phenyl rings only for ESEL ≥ 2.0, while for the triclinic modification the same procedure did not lead to a readable map. An E map calculated with ESEL ≥ 2.5 gave the positions of the triazine rings. The remaining C-atoms of the phenyl rings and the atoms of cyano groups were located successfully by difference Fourier synthesis. For the monoclinic modification all non-H atoms were refined anisotropically. The H-atoms were located from the $\Delta\rho$ maps, but in the final refinement they were fixed in their geometrical positions using HFIX 43 with the isotropic thermal parameters of $1.2 \times U_{eq}$ of the carbon atom linked directly to the H-atom. For the triclinic crystal the $\Delta\rho$ map led to the location of the atoms of the cyano groups for two with the three independent molecules of tris(2-cyanophenyl)-1,3,5-triazine. Successive difference Fourier maps showed that the cyano groups of the third molecule statistically occupied two positions; they are disordered. The hydrogen atoms were located in their geometrical positions. All non-H atoms, apart from the atoms of the disordered cyano groups of the one molecule, were refined anisotropically. Hydrogen atoms were fixed with $U_{iso} = 1.2 \times U_{eq}$, as for the monoclinic crystal. All details of the data collection and structure refinements are listed in Table 1.

Calculations. Ab-initio calculations were performed with the GAUSSIAN program package[47] at the Hartree–Fock level of theory. Full geometry optimizations were carried out with 6-31G(d) basis set functions starting from the X-ray structural geometry. As a convergence criterion the threshold limits of 0.00045 and 0.0018 a.u. were applied for the maximum force and displacement, respectively. 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.[48]

Bond critical points are 'saddle' points, in the electron density, along the bond between two atoms; they are often used to define the boundary between the bonded atoms.[49] At these saddle points (where $\nabla\rho = 0$), the three principal curvatures [the eingenvalues of the Hessian matrix of ρ (or $\nabla^2\rho$)] have one positive value and two negative values – (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_b at the bond critical point indicate the bond order; the ratio of the two negative curvatures define the bond ellipticity, ($\varepsilon = \lambda_1/\lambda_2 - 1$). The ellipticity is a measure of the π-character of bonds. The sum of the three curvatures (λ_1, λ_2 and λ_3) equals the Laplacian of ρ at r_b, and its sign determines the concentration of the charge density.[50] A negative value of the Laplacian $\nabla^2\rho(r_b)$ indicates that the charge density is concentrated at r_b, a positive value that the charge density is depleted at r_b. Analysis of the Laplacian distribution of ρ, through its local charge concentrations, provided a mapping of the free electron pair postulated in the Lewis model of the chemical bond.[51] The local maxima in the Laplacian function, i.e. (3, −3) critical points, are formed in the valence shell charge concentrations (VSCC) and the number is consistent with valence-shell electron pair repulsion theory (VSEPR).[52] Analysis of the Laplacian of the ρ function allows insight into the nature of the electronic structure of a molecule, as well as providing some information on the understanding of the reactivity of the molecule based on the charge density distribution in the molecule. Intermolecular interactions such as, e.g., hydrogen bonding and van der Waals interaction, are governed by the concentration of the charge density towards each interacting nucleus and lead to a positive value of the

Table 1. Crystal data, data collection conditions and refinement details.[a]

Formula		$(C_6H_4CN)_3C_3N_3$	
Colour		Colourless	Colourless
Mol. wt.		384.40	384.40
Crystal system		Monoclinic	Triclinic
Crystal size/mm		0.41 × 0.28 × 0.18	0.39 × 0.37 × 0.34
Space group		$P2_1/n$	$P1$
Unit cell dimensions:	*a*, *b*, *c*/Å	4.001(1), 23.852(5), 19.574(4)	11.276(2), 12.833(3), 12.915(3)
	α, β, γ/°	90.0, 94.61(3), 90.0	99.70(3), 112.31(3), 115.53(3)
Volume, *V*/Å		1861.9(7)	1431.4(5)
T/K		295(2)	295(2)
Z		4	3
F(000)		792	594
$D_{calc.}$/g cm^{-3}		1.371	1.338
$D_{obs.}$/g cm^{-3}		1.37	1.34
Radiation, Mo Kα/Å		0.71073	0.71073
2θ range/°		4–52	4–50
Index range:	*h*	0–4	−12–12
	k	−29–29	−15–15
	l	−12–23	−14–14
Reflections collected		6498	6707
Independent reflections		3234 ($R_{int.}$ = 0.0205)	6707
Observed reflections		2322 [$>2\sigma(I)$]	3777 [$>2\sigma(I)$]
Absorption coefficient, μ/mm^{-1}		0.086	0.086
Reference reflection		2 every 50, variation 1.1%	2 every 50, variation 0.8%
R for observed and all refl.		0.0687, 0.0924	0.0563, 0.1043
$wR(F^2)$ for observed and all refl.		0.1826, 0.2037	0.1437, 0.1728
Goodness-of-fit, *S*		1.041	0.971
Largest Δ/σ		0.001	0.038
Residual electron density (e Å^{-3})		+0.496, −0.208	+0.184, −0.149

[a] $R = \Sigma||F_o| - |F_c||/\Sigma F_o$; $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.1442P)^2 + 0.0166P$ where $P = (F_o^2 + 2F_c^2)/3$ for monoclinic and $w^{-1} = \sigma^2(F_o^2) + (0.1092P)^2 + 0.0000P$ where $P = (F_o^2 + 2F_c^2)/3$ for triclinic.

Laplacian function (i.e. the charge density is depleted in the interatomic surface). These topological definitions given above have a general character and illustrate topological behaviour of ρ and $\nabla^2\rho$ in the different kinds of chemical interaction and are helpful in understanding the phase transition from monoclinic to triclinic form in the crystal of tris(2-cyanophenyl)-1,3,5-triazine.

Discussion

The thermal trimerization of the 1,2-dicyanobenzene with the formation of the tris(2-cyanophenyl)-1,3,5-triazine requires a change in hybridization of the carbon atom from sp to sp^2 of only one of their two cyano groups. It is quite obvious that this process may compete with the main process of the formation of phthalocyanine.[4,31] The formation of tris(2-cyanophenyl)-1,3,5-triazine (as a by-product) during the synthesis of metallophthalocyanines, especially during the magnesium phthalocyanine synthesis may be connected with the formation of a complex of magnesium phthalocyanine with one molecule of 1,2-dicyanobenzene, as was suggested in Ref. 53. In this complex only one of the cyano groups of the 1,2-dicyanobenzene molecule is involved, which leaves the other free to rehybridization from sp to sp^2 and formation of tris(2-cyanophenyl)-1,3,5-triazine occurs.

The trimer of 1,2-dicyanobenzene has been proposed by several authors as a by-product of the synthesis of metallophthalocyanines, especially if the metal oxochloride was used, e.g. UO_2Cl_2[15] or $NbOCl_3$.[27] MacKay *et al.* who have studied some rare-earth phthalocyanines found it difficult to remove a white impurity (a by-product of the synthesis of gadolinium phthalocyanine from 1,2-dicyanobenzene and gadolinium chloride), which had a melting point of around 306 °C.[54] From the analysis of this white compound the authors suggested the empirical formula to be (1,2-dicyanobenzene)$_n$ polymer. We are convinced, that the white impurity observed by MacKay *et al.* is a trimer of 1,2-dicyanobenzene, since their IR spectrum is quite similar to the one obtained by us.

The IR spectrum of tris(2-cyanophenyl)-1,3,5-triazine shows the expected absorption band of the (C≡N) nitrile groups (see Fig. 1) at ≈2220 cm^{-1} in both crystalline (monoclinic and triclinic) modifications. The other absorption bands in the IR spectrum can be attributed to deformation of the triazine and benzene rings and to the stretching vibration of the C–C bonds between the triazine and phenyl rings. The stretching vibrations and the in-plane deformation of the C–H bonds of the phenyl rings are also observed in the IR spectrum. Since the IR spectra of both crystalline forms of the tris(2-cyanophenyl)-1,3,5-triazine were obtained from a Nujol mulls, in the IR spectra the bands at 1362, 1489, 2854 and a broad band at 2923 cm^{-1} are attributed to the Nujol vehicle. The Raman spectrum (see Fig. 2) of solid state tris(2-cyanophenyl)-1,3,5-triazine shows the band

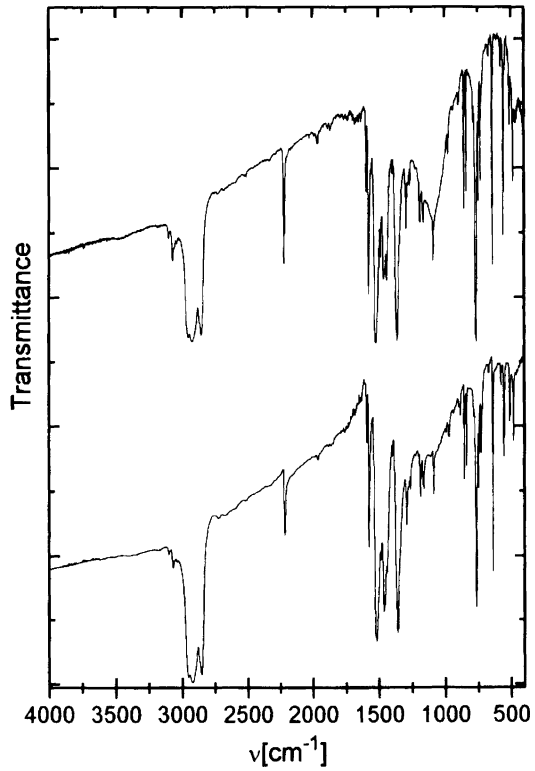

Fig. 1. IR spectra of tris(2-cyanophenyl)-1,3,5-triazine as Nujol mulls for the triclinic (top) and monoclinic form (bottom).

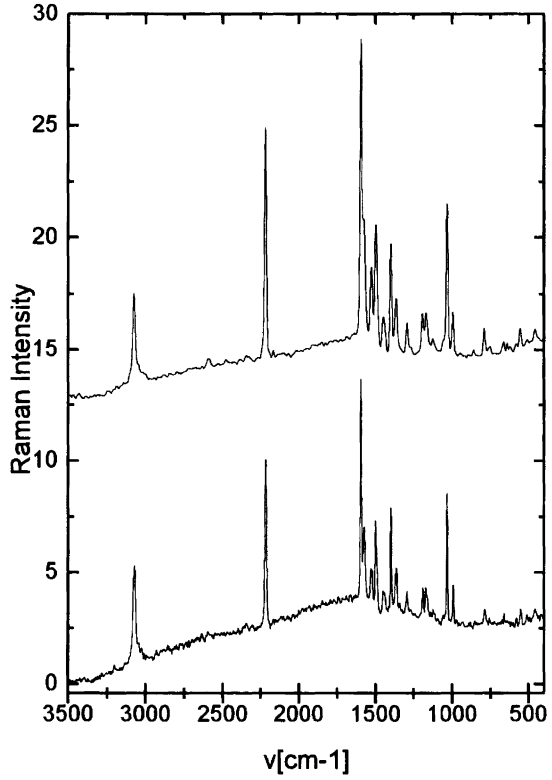

Fig. 2. Raman spectrum of solid state tris(2-cyanophenyl)-1,3,5-triazine for the triclinic (top) and monoclinic form (bottom).

due to the C≡N groups, but it is much more intense than that in the IR spectrum; this is typical for the nitrile groups. The other Raman bands can be attributed, similarly to the IR spectrum, to the triazine and phenyl rings. The IR and Raman frequencies are collected in Table 2.

The geometry of the tris(2-cyanophenyl)-1,3,5-triazine molecule in the monoclinic form (Fig. 3) is similar to two (M1 and M2) of the three independent molecules in the triclinic modification. The third independent molecule of tris(2-cyanophenyl)-1,3,5-triazine (M3) in the triclinic form has a disordered cyano groups. The tris(2-cyanophenyl)-1,3,5-triazine molecules in the both crystalline forms are not planar. The mean angle between the triazine and the phenyl rings is 8.3 and 6.3° in the monoclinic and triclinic forms, respectively.

The *ab-initio* fully optimized geometry of tris(2-cyanophenyl)-1,3,5-triazine at the HF/6-31G(d) level showed that tris(2-cyanophenyl)-1,3,5-triazine has C_3 symmetry, therefore the *ab-initio* calculation were also performed applying a three-fold axis at symmetry. The absolute energy calculated using the HF/6-31G(d) basis set was found to be −1235.5914 Hartree, and is a global

Table 2. Frequencies of the bands observed in the IR and Raman spectrum.

IR frequencies		Raman frequencies	
Monoclinic	Triclinic	Monoclinic	Triclinic
484w	485w	459w	458w
512w	510w	553w	555w
557m	552m	661w	663w
579w	580w	788w	790w
639s	640s	993w	994w
672w	671w	1032s	1033s
728w	728w	1172w	1170w
748m	748m	1191w	1191w
764vs	766vs	1295w	1295w
781w	788w	1365w	1365w
838m	840m	1399m	1398m
857m	857m	1451w	1448w
887w	899w	1500m	1496m
971w	976w	1522w	1525m
1091w	1091m	1530w	
1162w	1163w	1575m	1578m
1189w	1190w	1595vs	1594vs
1265w	1265w	2219[a]	2221s
1294m	1294m		2591w
1362s	1362s	3073m	3076m
1400w	1399w		
1465m	1442m		
1489s	1490m		
1522vs	1525vs		
1580m	1582m		
1595w	1595w		
2220w	2222m		
2853s	2855s		
2923s	2924s		
3070w	3070w		
3111w	3112w		

[a]w, weak; m, medium; s, strong; v, very.

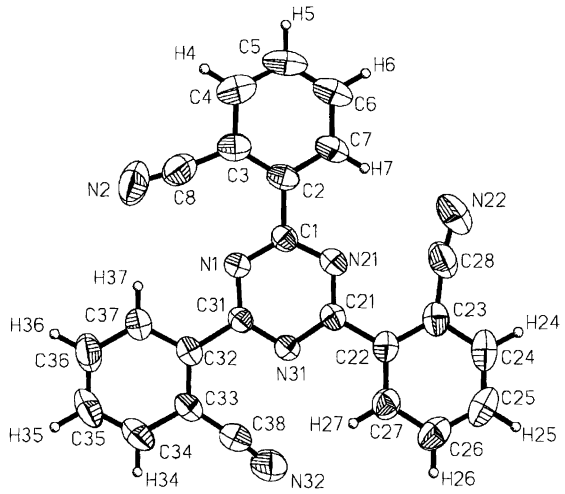

Fig. 3. View of tris(2-cyanophenyl)-1,3,5-triazine (monoclinic form) with atom labelling. Displacement ellipsoids are shown at the 50% probability level.

minimum on the potential energy surface (PES). The calculations exposed only one minimum energy on the PES. This energy minimum of the molecule fully correlates with the maximum delocalization of the π-electrons, not only in the phenyl and triazine rings, but as can be seen from the inter-ring C–C distances, also over the whole molecule (the bond order of these bonds is greater than 1). The geometrical parameters in optimized molecule are collected in Table 3, which also contains the average X-ray experimental parameters obtained for the monoclinic and triclinic forms. As can be seen from the Table 3, the bond lengths and angles in the optimized molecule are in sufficiently good agreement with those obtained from X-ray experiment. The experimental C–C bond distance between the phenyl ring and cyano group and C–C bond distance linking the triazine and phenyl rings are longer than these distances in the optimized molecule; this is probably due to the intermolecular interactions in the crystals. The difference in the torsion angles (around the C–C bond between the triazine and phenyl rings) between the optimized and experimental geometry of molecule is a consequence of the intramolecular electrostatic interaction between the nitrogen atom (N2) of the cyano groups and the hydrogen atom (H7) of the phenyl rings. The distance in the optimized molecule is 2.323 Å, while the average experimental distance is 2.55 and 2.40 Å for the monoclinic and triclinic forms, respectively. These weak hydrogen intramolecular interactions lead to the rotation of the all phenyl rings around the C–C bond between the phenyl and triazine rings, which leads to the planarity of the optimized molecule of tris(2-cyanophenyl)-1,3,5-triazine. The shortening of the C–C bond between the triazine and phenyl rings in the optimized molecule in relation to the experimental

Table 3. Optimized and experimental geometrical parameters for tris(2-cyanophenyl)-1,3,5-triazine.

		Experimental (X-ray single crystal)[a]				
			Triclinic			
Geometrical parameters (Å, °)	HF/6-31G(d)	Monoclinic	M1	M2	M3	Average
C1–N1	1.336	1.335	1.322	1.308	1.376	1.332
C1–N21	1.337	1.338	1.313	1.333	1.302	1.319
C1–C2	1.480	1.479	1.504	1.508	1.486	1.499
C2–C3	1.400	1.404	1.378	1.355	1.379	1.371
C3–C4	1.390	1.403	1.438	1.417	1.435	1.430
C4–C5	1.381	1.362	1.320	1.343	1.391	1.352
C5–C6	1.380	1.364	1.362	1.370	1.321	1.351
C6–C7	1.388	1.382	1.392	1.356	1.420	1.389
C7–C2	1.384	1.396	1.414	1.421	1.409	1.415
C3–C8	1.433	1.451	1.496	1.499	1.487	1.494
C8–N2	1.152	1.156	1.186	1.159	1.154	1.166
N1–C1–N21	121.97	124.6	124.1	127.4	125.1	125.5
C1–N1–C31	118.03	115.4	115.9	112.6	114.9	114.5
N1–C1–C2	120.21	118.3	119.1	118.8	116.3	118.1
C1–C2–C3	123.19	122.5	122.3	122.7	124.2	123.1
C2–C3–C4	119.65	119.1	120.7	120.6	120.0	120.4
C3–C4–C5	120.78	121.3	116.3	116.0	114.6	115.6
C4–C5–C6	119.65	119.7	125.9	123.1	126.0	125.0
C5–C6–C7	120.08	120.5	119.7	121.5	119.1	120.1
C6–C7–C2	121.02	121.1	118.4	118.6	118.2	118.4
C3–C2–C7	118.82	118.2	119.2	119.8	119.0	119.3
C2–C3–C8	124.91	125.5	123.6	126.3	125.5	125.8
C3–C8–N2	174.94	173.4	171.1	171.8	170.6	171.2
N1–C1–C2–C3	0.02	8.3	7.1	7.0	4.6	6.3

[a]E.s.d.s: bond lengths, 0.002–0.004 Å; bond angles, 0.2–0.3° (monoclinic); bond lengths, 0.007–0.016 Å; bond angles, 0.5–1.5° (triclinic).

Table 4. Charge density topological parameters for the optimized geometry of tris(2-cyanophenyl)-1,3,5-triazine [HF/6-31G(d)].

Bond	Length	ρ/e Å^{-3}	$\nabla^2\rho$/e Å^{-5}	λ_1	λ_2	λ_3	ε	AT1-CP/Å	CP-AT2/Å
C1-N1	1.336	2.226	−19.333	−16.52	−16.39	13.58	0.007	0.504	0.839
C1-N21	1.337	2.138	−17.967	−15.47	−15.40	12.90	0.005	0.510	0.832
C1-C2	1.480	1.724	−17.060	−11.65	−10.87	5.46	0.072	0.789	0.691
C2-C3	1.400	1.970	−20.777	−13.51	−11.57	4.30	0.170	0.674	0.726
C3-C4	1.390	2.013	−21.470	−13.90	−11.99	4.42	0.160	0.735	0.655
C4-C5	1.381	2.049	−22.566	−14.17	−12.50	4.11	0.134	0.703	0.678
C5-C6	1.380	2.053	−22.651	−14.19	−12.57	4.13	0.129	0.701	0.679
C6-C7	1.388	2.047	−22.611	−14.09	−12.61	4.08	0.118	0.692	0.694
C7-C2	1.384	2.025	−21.776	−13.82	−12.28	4.33	0.125	0.654	0.734
C3-C8	1.433	1.773	−16.410	−11.24	−11.16	5.99	0.007	0.606	0.829
C8-N2	1.152	3.246	−12.321	−28.73	−28.69	45.10	0.001	0.419	0.733
C4-H4	1.071	1.853	−20.198	−16.26	−16.23	12.29	0.002	0.683	0.388
C5-H5	1.071	1.846	−20.093	−16.16	−16.06	12.13	0.004	0.681	0.390
C6-H6	1.070	1.851	−20.165	−16.24	−16.19	12.27	0.004	0.683	0.388
C7-H7	1.069	1.900	−20.232	−17.58	−17.54	13.89	0.002	0.698	0.369

geometry is a consequence of its planarity and the possibility of overlap between the p_z orbitals of both carbon atoms (this is also evident in the topological parameters of the bond CP, especially the ellipticity – see Table 4).

The charge density at the bond CPs correlates with the corresponding bond lengths and has been used for the calculation of the bond order.[55,56] The π-character bonds are especially good in the phenyl rings (ε= 0.118–0.170) as a result the delocalization of the π-electrons. The asymmetric location of the bond CPs in the triazine ring is correlated with the polar character of the C–N bonds. The fact that the location of the bond CP correlates with the polar character of the bond has been used as a measure of the bond polarity.[57] The C–N bond lengths in the triazine ring are shorter than those in unsubstituted triazine molecule[58] and are comparable to those in other triazine derivatives.[59–67] The N–C–N

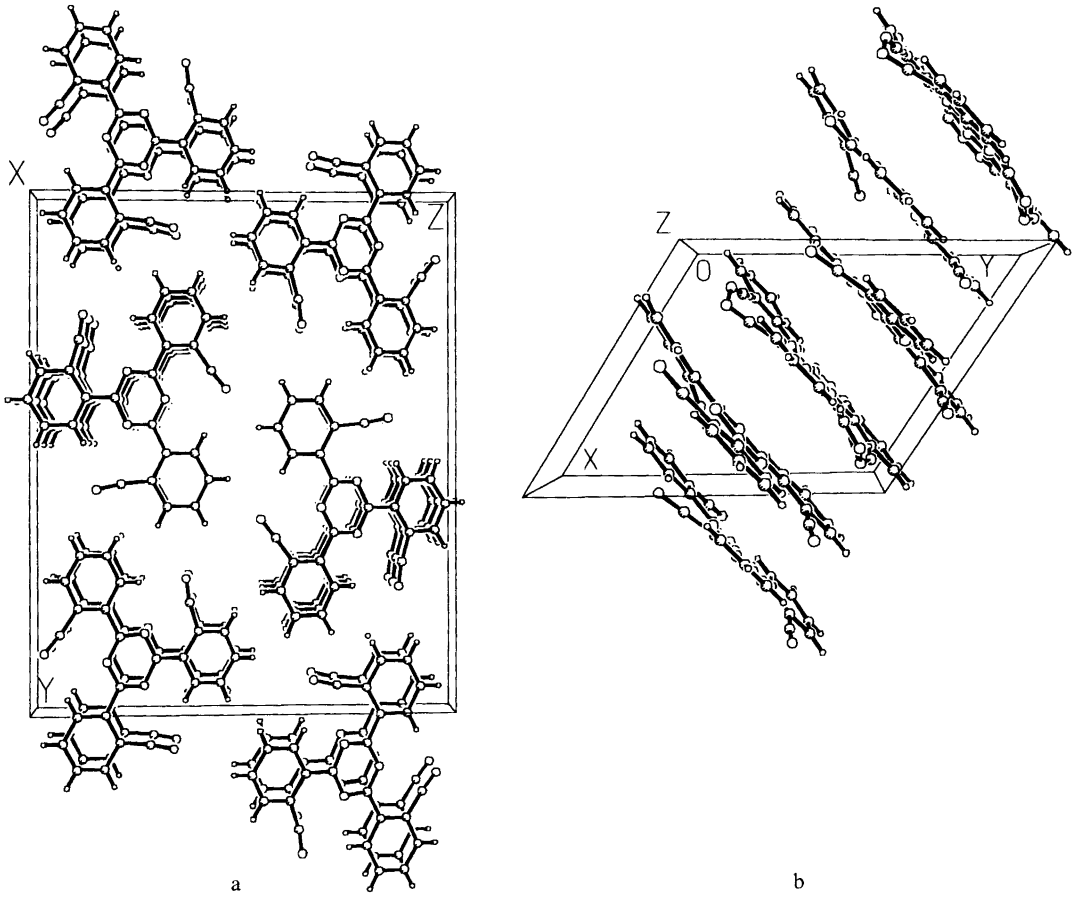

Fig. 4. Molecular architecture of the (a) monoclinic and (b) triclinic form of tris(2-cyanophenyl)-1,3,5-triazine.

angles in the triazine ring are larger than 120°, the other C–N–C angles are smaller than 120°. This relation is typical for unsubstituted and substituted triazine molecules.

The molecular arrangement in the unit cell are presented in Fig. 4a and b. The tris(2-cyanophenyl)-1,3,5-triazine molecules in the both crystalline forms are almost parallel. The distance between the average plane of the two neighbouring molecules in the monoclinic form is 3.21(1) Å, while in the triclinic form it is 3.02(1), 3.37(1) and 3.43(1) Å between the M1 and M3, M3 and M2, and M1 and M2 neighbouring molecules, respectively. If we assign the symbol A to both molecules M1 and M2, and B to the molecule with the disordered of cyano groups, the arrangement sequence of the molecules in the triclinic modification can be written as ABAABA....

The phase transition in the crystal of tris(2-cyanophenyl)-1,3,5-triazine from monoclinic to triclinic may be explained as follows. In phase I (monoclinic) the molecules are arranged in columnar stacks almost parallel to the *b*-axis and adopt only one molecular orientation in the stacks (Fig. 4a). This is stable up to $\approx$270 °C. At higher temperatures the π-character of the C–C bonds connecting the triazine and the phenyl rings (see Table 4, the ellipticity of this C–C bond is 0.072) is interrupted (as a consequence the increased energy of the molecule) and only flexible single σ C–C bonds then exist. This allows rotation around the σ C–C bonds of the 2-cyanophenyl subunits in the one of the three independent tris(2-cyanophenyl)-1,3,5-triazine molecules. Additionally, the molecules that overlapped rigidly in the molecular stacks of the monoclinic form, in phase II (triclinic) are shifted as a result the reorientation of the 2-cyanophenyl subunits (Fig. 4b).

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