

# A New Crystalline ( $\alpha$ ) Form of 1,4-Dicyanobenzene

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Kubiak, R. and Janczak, J., 1996. A New Crystalline ( $\alpha$ ) Form of 1,4-Dicyanobenzene. – Acta Chem. Scand. 50: 1164–1167. ©Acta Chemica Scandinavica 1996.

1,4-Dicyanobenzene is dimorphous, crystallizing in both triclinic ( $\beta$ ) and monoclinic ( $\alpha$ ) form. The triclinic form is transformed into the monoclinic above 430 K. Single crystals of the latter have been obtained and its structure determined at room temperature. The cell dimensions are  $a=3.868(1)$ ,  $b=7.080(1)$ ,  $c=12.127(2)$  Å,  $\beta=97.21(3)^\circ$ ,  $V=329.48(11)$  Å<sup>3</sup>, space group  $P2_1/c$ ;  $Z=2$ . The structure was solved by direct methods and 54 parameters refined on  $F$  to  $R=0.050$ ,  $wR=0.061$  and  $S=1.29$  for 535 observed reflections ( $F>4\sigma_{(f)}$ ) measured in the range  $4\leq 2\theta\leq 60$  (Mo  $K\alpha$  radiation). The details of the  $\alpha$ -form crystal structure are discussed and compared with the  $\beta$ -form described in the literature.

This X-ray crystallographic study of 1,4-dicyanobenzene (1,4-DCB) was undertaken to complete the crystal structure information on dicyanobenzenes and to provide a basis for further synthesis work in our laboratory. Recently we determined the crystal structure of 1,2-dicyanobenzene,<sup>1</sup> which we are using for the synthesis of metallophthalocyanines.<sup>2,3</sup> Moreover, during our studies we found that, depending on the reaction conditions, both or only one cyano group of 1,2-DCB is transformed, leading, respectively, to tetramerization and a molecular precursor of phthalocyanines, or to trimerization and a triazine derivative.

A similar cyclization reaction of 1,4-DCB cannot yield a chelate-forming molecule of type **1**, but one may expect that the formation of an appropriate analog of molecule **2** should be possible. We therefore decided to start by investigating how the crystal structure of 1,4-DCB<sup>4,5</sup> changes upon heating below the melting temperature. Here we present the results obtained by X-ray diffraction studies of powder and single-crystal 1,4-DCB samples.

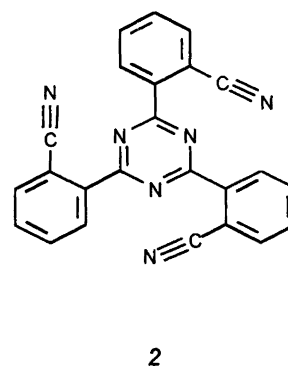
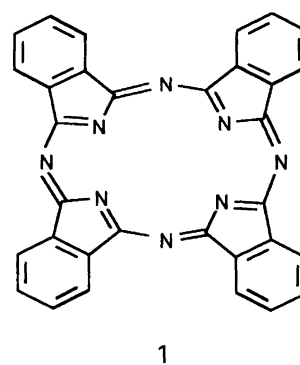
## Experimental

The polycrystalline sample and the single crystals used in these experiments were prepared from 1,4-DCB purchased from Aldrich (melting point 497–500 K).

*X-Ray powder measurements.* The powder diffraction records, using Cu  $K\alpha$  radiation, were obtained with a Siemens D-5000 powder diffractometer equipped with an A. Paar He-TTK temperature attachment working under dynamic vacuum. The 1,4-DCB sample was therefore

compacted into a pellet and covered with Kapton foil in order to prevent evaporation. Recordings were made at several temperatures, between 298 and 460 K.

*Single crystal growth.* Single crystals of 1,4-DCB were grown by evaporation and condensation of polycrystal-



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line 1,4-DCB in evacuated and sealed glass ampoules. The ampoule was placed in a temperature-gradient furnace with its cooler end at about 440 K. After one day the ampoule was removed and cooled in air. In this manner parallelepipedic colourless crystals up to 1 mm thick were obtained. An analysis of the crystals carried out on an energy dispersive spectrometer (EDAX) showed no composition change from the polycrystalline starting 1,4-DCB sample.

**X-Ray data collection.** A colourless parallelepipedic single crystal of the  $\alpha$ -form 1,4-dicyanobenzene, of approximate dimensions  $0.40 \times 0.40 \times 0.22$  mm, was used for data collection on a four-circle Kuma Diffraction KM-4 diffractometer with graphite-monochromatized Mo K $\alpha$  radiation. Preliminary examination of the crystal by rotation and Weissenberg photographs indicated monoclinic symmetry. The orientation matrices and unit-cell dimensions were refined by a least-squares fit of 20 accurately centered reflections measured in the range  $16 \leq 2\theta \leq 23^\circ$ . A total of 1612 reflections were measured in the range  $4 \leq 2\theta \leq 60^\circ$ , using the  $\omega/2\theta$  scan technique. Two standard reflections were monitored every 50

recordings, showing no significant intensity variations. Intensities and their standard deviations were corrected for Lorentz and polarization effects, and 825 independent reflections ( $535$  with  $F > 4\sigma$ ),  $R_{\text{int}} = 0.0317$ , were used for crystal structure solution and refinement.

**Structure determination and refinement.** The structure was solved by direct methods. Initially the structure was refined with isotropic, then anisotropic temperature factors by full-matrix least-squares techniques, using the SHELXTL program system.<sup>6</sup> A difference Fourier synthesis showed maxima in positions consistent with the expected locations of the H atoms. The positional and displacement parameters for the H atoms were refined. The function minimized was  $\sigma_w(|F_o| - |F_c|)^2$  with the weighting scheme  $w = 1/(\sigma^2 + 0.001F^2)$ . The final unweighted and weighted agreement factors converged to  $R = 0.050$  and  $wR = 0.061$ ; a goodness-of-fit calculation resulted in a value of 1.29 at final convergence. The final difference map calculation showed no peaks of chemical significance; the largest were  $+0.13$  and  $-0.28$  e  $\text{\AA}^{-3}$ . Scattering factors for neutral atoms and calculations for anomalous dispersion were as in SHELXTL, which was used for all the crystal structure calculations and drawings. Details of the data collection parameters, crystal data and final agreement factors are collected in Table 1. The final positional coordinates and equivalent isotropic thermal parameters are given in Table 2. Bond lengths and angles are collected in Table 3.

Table 1. Crystallographic data for 1,4-dicyanobenzene.

Formula	C <sub>6</sub> H <sub>4</sub> (CN) <sub>2</sub>
Color	Colorless
Mol. wt.	128.1
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions	<i>a</i> = 3.868(1) Å <i>b</i> = 7.080(2) Å <i>c</i> = 12.127(3) Å $\beta$ = 97.21(3)° <i>V</i> = 329.48(11) Å <sup>3</sup>
Volume	2
<i>Z</i>	132
<i>F</i> (000)	1.292
<i>D</i> <sub>calc.</sub>	1.29
<i>D</i> <sub>obs.</sub> (flotation)/g cm <sup>-3</sup>	Mo K $\alpha$
Radiation	Kuma Diffraction KM-4
Diffractometer	Variable, 0.02–0.12
Scan speed/deg min <sup>-1</sup>	0.8 + tg $\theta$
Scan width/deg	4–60
2 $\theta$ range	0 ≤ <i>h</i> ≤ 5, −9 ≤ <i>k</i> ≤ 9, −14 ≤ <i>l</i> ≤ 16
Index range	1612
Reflections collected	825 ( $R_{\text{int}} = 0.0317$ )
Independent reflections	535 ( $F > 4\sigma(F)$ )
Observed reflections	2 measured every 50
Standard reflections	9.9
Data/LS parameters	0.076
Absorption coefficient, $\mu/\text{mm}^{-1}$	Lorentz, polarization, no absorption
Correction	0.050, 0.061
<i>R</i> and <i>wR</i> for observed reflections	0.081, 0.072
<i>R</i> and <i>wR</i> for all measured reflections	1.29
Goodness-of-fit	0.001
Largest $\Delta/\sigma$	+0.13, −0.28
Residual electron density/e $\text{\AA}^{-3}$	

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $10^4 \text{\AA}^2$ ).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>a</sup>
C(1)	2820(5)	1683(3)	1016(2)	560(6)
C(2)	1372(4)	3381(2)	489(1)	473(5)
C(3)	1262(5)	3598(2)	−644(2)	531(5)
C(4)	105(5)	4773(3)	1137(2)	535(6)
N(1)	4008(5)	367(2)	1440(2)	744(7)
H(3)	2179(49)	2681(25)	−1092(15)	570(50)
H(4)	160(57)	4549(26)	1922(17)	790(60)

<sup>a</sup> *U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor (for C and N atoms).

Table 3. Bond lengths (in Å) and bond angles (in deg).<sup>a</sup>

C(1)–N(1)	1.133(2)
C(1)–C(2)	1.441(2)
C(2)–C(3)	1.378(3)
C(2)–C(4)	1.378(2)
C(3)–C(4A)	1.374(2)
C(4)–C(3A)	1.374(2)
C(2)–C(1)–N(1)	178.7(2)
C(1)–C(2)–C(4)	119.1(2)
C(1)–C(2)–C(3)	119.8(2)
C(3)–C(2)–C(4)	121.11(1)
C(2)–C(3)–C(4A)	119.3(2)
C(2)–C(4)–C(3A)	119.2(2)

<sup>a</sup> Symmetry code: *A*,  $-x, 1-y, -z$ .

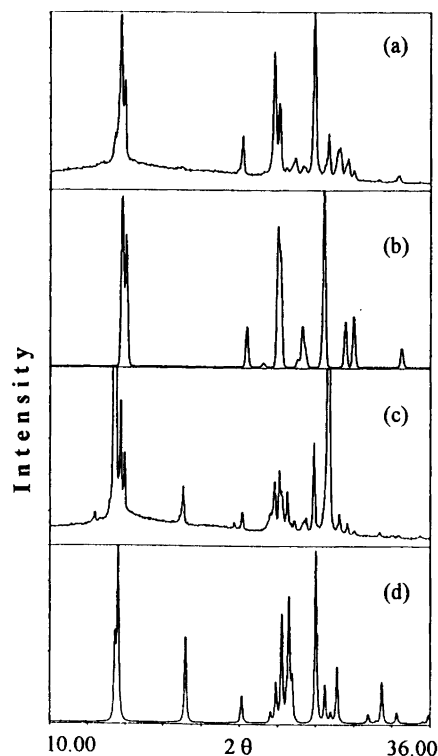


Fig. 1. The powder diffraction pattern for 1,4-dicyanobenzene: (a) triclinic ( $\beta$ ) form measured at 420 K; (b) calculated for triclinic ( $\beta$ ) form (Ref. 5); (c) monoclinic ( $\alpha$ ) form measured at 430 K; (d) calculated for monoclinic ( $\alpha$ ) form.

## Results and discussion

X-Ray powder diagrams of 1,4-dicyanobenzene samples taken at several temperatures between room temperature and 420 K were practically unchanged except for temperature expansion. As may be seen from a comparison of the recorded powder diffraction diagram, presented in Fig. 1(a), and one [Fig. 1(b)] calculated from the crystal structure of 1,4-DCB given in Ref. 5, this crystal structure ( $\beta$ -form) is preserved at least up to 420 K. However, the powder diffraction diagram taken at 430 K [Fig. 1(c)] shows new diffraction lines at changed positions, indicating the existence of another phase ( $\alpha$ -form) in the 1,4-DCB sample. We proved that this phase transition is

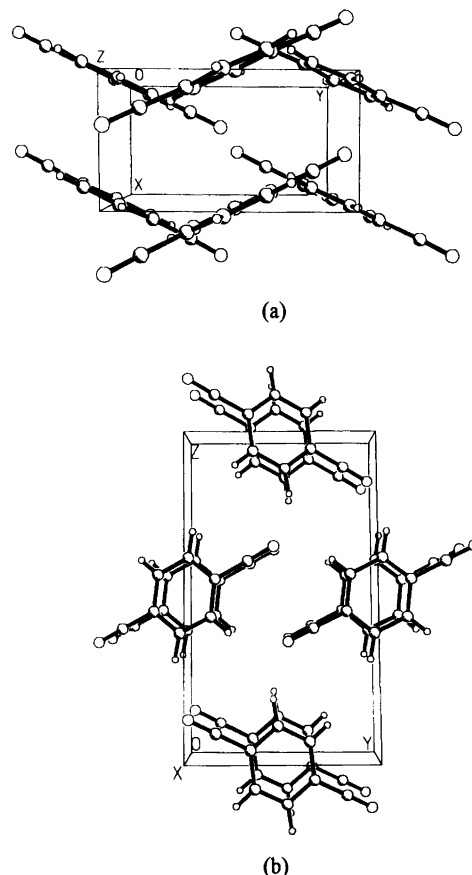


Fig. 3. Packing of the 1,4-DCB molecules in the unit cell shown by (a) an  $ac$  projection and (b) a  $bc$  projection.

reversible, although the  $\alpha$  form can be easily supercooled. Therefore we were able to perform a single-crystal X-ray investigation of the  $\alpha$ -form at room temperature, i.e., in a metastable state. As can be seen from Fig. 1(d), the diagram calculated for the  $\alpha$ -form (cell parameters and atomic coordinates obtained from single-crystal data) agrees very well with that measured for a polycrystalline sample at 430 K.

The relationship between the triclinic and monoclinic forms of 1,4-dicyanobenzene is quite analogous to that found between  $\beta$ - and  $\alpha$ -1,4-dichlorobenzene.<sup>7</sup> In the

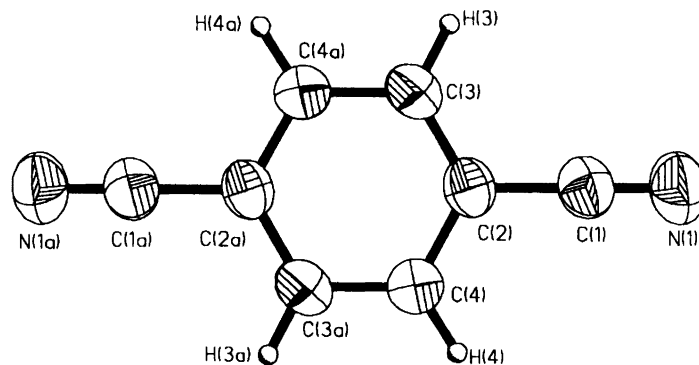


Fig. 2. View of the molecular structure of 1,4-dicyanobenzene with the atom numbering.

triclinic form, the sheets formed by 1,4-DCB or 1,4-dichlorobenzene molecules are translationally identical, whereas in monoclinic forms adjacent sheets are correlated by a twofold screw axis. The molecular structure (see Figs. 2 and 3) of 1,4-DCB in the  $\alpha$ -form does not deviate significantly from that found in the  $\beta$ -form.<sup>4,5</sup> The bond lengths in the benzene ring found by us ( $\alpha$ -form) are on average 0.006 Å shorter than the corresponding bond lengths in the  $\beta$ -form.<sup>4,5</sup> The corresponding angles are the same in both forms to within standard deviations. The most appreciable difference was found in the bond distance C–CN, which is significantly longer in the  $\beta$  [1.145(2) Å] than in the  $\alpha$ -form [1.133(2) Å]. Consequently the N···H intermolecular contacts involving cyano groups present in the  $\beta$ -form (2.61 Å, Ref. 5), do not exist in the  $\alpha$ -form [2.772(5) Å].

*Acknowledgements.* The authors would like to thank Professor Z. Gałdecki from Technical University of Łódź,

Poland, for the opportunity to use the SHELXTL/PC program system in his laboratory.

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Received May 13, 1996.