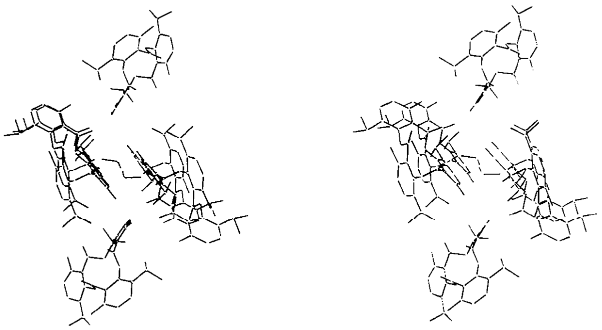

Fig. 4. A stereoscopic view along the twofold axis of the six proximal (*M*)-TOT molecules contributing to the formation of the cage. For clarity only the *R* enantiomer of 2-bromobutane is shown (the left rear molecule is the TOT molecule whose coordinates are listed in Table 1).

cage whose twofold symmetry has been clearly established. Secondly, the *R* factor for symmetry $P3_121$ could be substantially lowered, in a somewhat artificial manner, by fixing the Br atom on the twofold axis (this implies only a small conformational distortion) and refining its temperature factor anisotropically. The overall scale factor was also adjusted while the rest of the asymmetric unit was kept invariant. Following this procedure the *R* factor dropped from 0·081 to 0·067, in qualitative agreement with the strongly anisotropic contribution of the Br atom to the scattering of the disordered guest molecule.* This demonstrates how static disorder can be mimicked by a magnified thermal motion. The elongated electron density distribution at the Br site (Fig. 3) is due to the weighted overlap of four atoms displaced from each other and related in pairs by the twofold axis. Each pair of equivalent atoms is associated with one of the enantiomers of 2-bromobutane. However, the minor enantiomer, (*S*)-2-bromobutane, has not been experimentally located. Its calculated orientation, fitting the minimum of the van der Waals energy in a rigid cage (Gerdil & Allemand, 1980), is depicted in Fig. 3.

According to the NMR and chiroptical observations the situation prevailing in a single crystal can be roughly described as follows: the cavities are vacant in the ratio 1:4 and the same enantiomer is present in two out of three filled cavities. *The introduction of an occupancy factor of 0·75, and of a $\frac{1}{3}$ contribution of the S enantiomer in the refinement did not, however, bring about any significant improvement.* Inspection of the host–guest intermolecular contacts suggests that the enclosed component fits tightly into the cage and has only little motional freedom. A detailed analysis of the host–guest interactions will be presented elsewhere together with that for related clathrates [see preliminary account (Gerdil & Allemand, 1980)]. A stereoscopic view of the packing arrangement is shown in Fig. 4.

Financial support for this work by the Swiss National Science Foundation is gratefully acknowledged.

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* In addition to any dynamic disorder there are two kinds of static disorder which severely impair the precise localization of the guest atoms: (i) two enantiomeric molecules are present (enantiomeric excess = 35%); (ii) the distribution of the atoms must conform with the twofold symmetry.

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The Structures of *m*-Cyanoaniline and *p*-Cyanoaniline*

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Abstract

m-Cyanoaniline, $C_7H_6N_2$, $M_r = 118{\cdot}14$, is orthorhombic, $Pna2_1$, with $Z = 4$, $a = 8{\cdot}27$ (1), $b = 16{\cdot}94$ (2), $c = 4{\cdot}89$ (1) Å, $V = 685{\cdot}1$ Å^3, $D_c = 1{\cdot}14$ g cm^{-3}, μ(Cu $K\alpha$) = 5·9 cm^{-1}. *p*-Cyanoaniline, $C_7H_6N_2$, $M_r = 118{\cdot}14$, is monoclinic, $P2_1/c$, with $Z = 4$, $a = 7{\cdot}35$ (1), $b = 5{\cdot}56$ (1), $c = 16{\cdot}10$ (2) Å, $\beta = 102{\cdot}0$ (1)°, $V = 643{\cdot}6$ Å^3, $D_c = 1{\cdot}22$ g cm^{-3}, μ(Cu $K\alpha$) = 6·3 cm^{-1}.

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* 3- and 4-aminobenzonitrile.

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The two structures were solved by direct methods and refined by the least-squares procedure to $R = 0{\cdot}065$ for 548 observed reflections and to $R = 0{\cdot}068$ for 768 observed reflections respectively. The molecular features and the hydrogen-bonding systems are described and compared.

Introduction

Nuclear quadrupole resonance (NQR) measurements, made on two series of *para* and *meta* derivatives of cyanoaniline (Colligiani, Ambrosetti, Angelone & Oja, 1975), indicated anomalies in the quadrupole parameters of the ^{14}N nucleus of the cyano group when the *para* or the *meta* substituent was an amino or hydroxyl group. An analysis of the electron populations in the bonding orbitals of the ^{14}N atom in the cyano group, made on the basis of the theory of Townes & Dailey (1949), indicated that the anomalies could be due to intermolecular hydrogen bonds involving the lone-pair orbitals in the cyano group and the protons in the amino and hydroxyl groups.

The NQR data gave strong indications that two nearly equivalent bonds were formed in *m*-cyanoaniline while only one was probably present in *p*-cyanoaniline. This prompted us to determine the crystal structures of *m*-cyanoaniline (MCA) and *p*-cyanoaniline (PCA) to test those indications and to compare the molecular and crystal structures of the two compounds.

Experimental

Small crystals were used for the intensity-data collection. The data were recorded with Ni-filtered Cu $K\alpha$ radiation on Weissenberg photographs, with the multiple-film technique and integration procedure. For MCA five layers with c as rotation axis ($l = 0$ through 4) were recorded and 548 independent reflections were observed. For PCA six layers with b as rotation axis ($k = 0$ through 5) were recorded and 768 independent reflections were observed. The intensities were measured with a Nonius microdensitometer and corrected for Lorentz and polarization factors, and α_1–α_2 spot doubling; no correction was made for absorption because of the low values of the absorption coefficients.

By means of the *DATFIX* program incorporated in XRAY 70 (Stewart, Kundell & Baldwin, 1970) overall isotropic temperature factors, scale factors and normalized structure factor magnitudes E for both structures were calculated. For MCA the statistical averages and distribution of E indicated a non-centrosymmetric distribution of atoms in the unit cell: the space group $Pna2_1$ was thus assumed.

Table 1. *Final positional* ($\times 10^4$; *for* H $\times 10^3$) *and thermal parameters with estimated standard deviations in parentheses*

$$B_{\rm eq} = \tfrac{4}{3} \textstyle\sum_i \sum_j \beta_{ij}\, \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	y	$B_{\rm eq}$ (Å^2)
MCA				
C(1)	2752 (6)	5518 (2)	2807 (24)	2·69
C(2)	2923 (5)	6258 (3)	1493 (25)	3·09
C(3)	1909 (6)	6899 (2)	2300 (26)	3·16
C(4)	755 (7)	6808 (3)	4334 (27)	3·92
C(5)	621 (7)	6063 (3)	5608 (28)	4·33
C(6)	1608 (7)	5435 (3)	4867 (28)	3·47
C(7)	2038 (7)	7640 (3)	797 (28)	4·50
N(1)	3812 (6)	4901 (2)	2100 (26)	4·14
N(2)	2167 (7)	8240 (3)	−311	6·98
H(1)	366	637	−20	
H(2)	12	730	480	
H(3)	−12	603	767	
H(4)	141	503	600	
H(5)	415	495	−13	
H(6)	361	450	223	
PCA				
C(1)	2791 (4)	6362 (5)	7164 (2)	4·68
C(2)	3540 (5)	7235 (6)	6494 (2)	5·02
C(3)	3294 (5)	6008 (6)	5736 (2)	4·95
C(4)	2294 (4)	3828 (5)	5630 (2)	4·66
C(5)	1540 (5)	2966 (6)	6290 (2)	5·05
C(6)	1770 (5)	4185 (6)	7045 (2)	5·02
C(7)	2123 (5)	2482 (7)	4860 (3)	5·89
N(1)	3042 (5)	7549 (7)	7918 (3)	6·31
N(2)	2037 (5)	1355 (7)	4260 (2)	7·31
H(1)	448	853	653	
H(2)	388	668	527	
H(3)	70	141	624	
H(4)	137	365	749	
H(5)	379	888	800	
H(6)	268	707	833	

The structures were solved by direct methods; three-dimensional E maps, calculated with about 100 of the highest E values, whose phases were determined using *MULTAN* (Main, Woolfson & Germain, 1971), clearly showed the positions of all the C and N atoms in the structures.

Full-matrix least-squares refinement cycles reduced $R = \sum ||F_o| - |F_c||/\sum |F_o|$ to 0·144 for MCA and to 0·148 for PCA; individual isotropic temperature factors and scale factors were among the refined parameters. Two refinement cycles with anisotropic temperature factors reduced R to 0·103 and 0·109 respectively. Three-dimensional difference Fourier syntheses calculated at this stage revealed the positions of the H atoms. Full-matrix least-squares refinement cycles were then made with anisotropic temperature factors for the C and N atoms, and isotropic temperature factors for the H atoms; the H-atom positions were held fixed for PCA, but allowed to vary for MCA. The weighting scheme used in the final cycles was $\sqrt{w} = 1/(a + |F_o| + b|F_o|^2)$, where $a = 2{\cdot}7$, $b = 0{\cdot}08$ for MCA, and $a = 1{\cdot}5$, $b = 0{\cdot}05$ for PCA. Refinements were concluded at $R = 0{\cdot}065$ and $0{\cdot}068$

respectively. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Final positional parameters are given in Table 1.*

Discussion

The geometry and atom numbering for MCA and PCA are shown in Figs. 1 and 2 respectively (*ORTEP*; Johnson, 1965). The bond lengths and angles are given in Table 2. The equation of the least-squares plane through the six C atoms of the ring and the displacements of all the non-hydrogen atoms from this plane are given in Table 3.

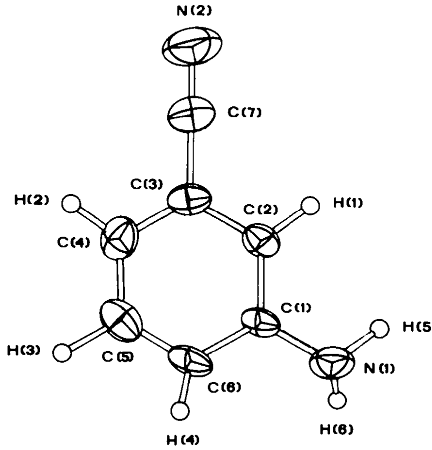

Fig. 1. *ORTEP* drawing of MCA projected down a direction perpendicular to the benzene-ring plane. Anisotropic thermal parameters are represented at the 50% probability level, while hydrogen thermal parameters are spheres of arbitrary size.

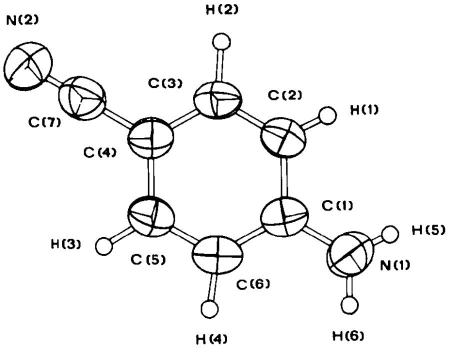

Fig. 2. *ORTEP* drawing of PCA projected down a direction perpendicular to the benzene-ring plane. Anisotropic thermal parameters are represented at the 50% probability level, while hydrogen thermal parameters are spheres of arbitrary size.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

MCA

C(1)–C(2)	1·416 (9)	C(1)–C(2)–C(3)	119·3 (8)
C(2)–C(3)	1·427 (8)	C(2)–C(3)–C(4)	121·2 (6)
C(3)–C(4)	1·387 (14)	C(3)–C(4)–C(5)	118·0 (6)
C(4)–C(5)	1·411 (11)	C(4)–C(5)–C(6)	121·6 (9)
C(5)–C(6)	1·389 (9)	C(5)–C(6)–C(1)	120·8 (7)
C(6)–C(1)	1·389 (14)	C(6)–C(1)–C(2)	119·2 (5)
C(3)–C(7)	1·459 (11)	C(2)–C(3)–C(7)	118·2 (9)
C(7)–N(2)	1·157 (9)	C(4)–C(3)–C(7)	120·5 (5)
C(1)–N(1)	1·408 (7)	C(3)–C(7)–N(2)	177·4 (1·1)
		C(2)–C(1)–N(1)	119·0 (8)
		C(6)–C(1)–N(1)	121·8 (7)

PCA

C(1)–C(2)	1·396 (5)	C(1)–C(2)–C(3)	120·8 (3)
C(2)–C(3)	1·377 (5)	C(2)–C(3)–C(4)	120·1 (3)
C(3)–C(4)	1·410 (4)	C(3)–C(4)–C(5)	119·2 (3)
C(4)–C(5)	1·382 (5)	C(4)–C(5)–C(6)	121·0 (3)
C(5)–C(6)	1·371 (5)	C(5)–C(6)–C(1)	120·4 (3)
C(6)–C(1)	1·416 (4)	C(6)–C(1)–C(2)	118·4 (3)
C(4)–C(7)	1·430 (5)	C(3)–C(4)–C(7)	120·3 (3)
C(7)–N(2)	1·143 (5)	C(5)–C(4)–C(7)	120·5 (3)
C(1)–N(1)	1·360 (5)	C(4)–C(7)–N(2)	177·6 (4)
		C(2)–C(1)–N(1)	121·2 (3)
		C(6)–C(1)–N(1)	120·3 (4)

Table 3. *Deviations from the benzene-ring plane* (Å)

The equations of the least-squares plane through the six C atoms of the ring, referred to the crystallographic axes, are: $5{\cdot}5794x + 4{\cdot}7040y + 3{\cdot}3443z = 5{\cdot}0770$ for MCA and $5{\cdot}7875x - 2{\cdot}8396y + 2{\cdot}7998z = 1{\cdot}8113$ for PCA.

MCA (average e.s.d. in the atom displacement is 0·008 Å)

C(1)*	−0·004	N(1)	0·060
C(2)*	−0·002	C(7)	−0·077
C(3)*	0·004	N(2)	−0·096
C(4)*	−0·001		
C(5)*	−0·005		
C(6)*	0·008		

PCA (average e.s.d. in the atom displacement is 0·003 Å)

C(1)*	0·003	N(1)	0·023
C(2)*	0·001	C(7)	0·073
C(3)*	−0·005	N(2)	0·175
C(4)*	0·005		
C(5)*	−0·001		
C(6)*	−0·003		

* Atoms defining the least-squares plane.

The geometrical deformations induced in the benzene nucleus by substituents have been studied in a number of papers (Domenicano, Vaciago & Coulson, 1975*a*,*b*, and references therein): a large mass of structural data indicated that in *para*- or *meta*-substituted benzene derivatives the value of the internal angle at the *ipso* atom, α, associated with a given functional group, is not affected by *para* or *meta* substitution (Domenicano, Vaciago & Coulson, 1975*a*;

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36567 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Domenicano, Mazzeo & Vaciago, 1976). In this context it seems noteworthy that the values of α_{CN}, 121·2°, and α_{NH_2}, 119·2°, in MCA compare well with the corresponding values in benzonitrile, 121·8°, (Casado, Nygaard & Sørensen, 1971) and aniline, 119·4°, (Lister, Tyler, Høg & Wessel Larsen, 1974), determined by microwave spectroscopy. Moreover, C(3)–C(7), 1·459 Å, and C(1)–N(1), 1·408 Å, in MCA compare well with the corresponding bond lengths in benzonitrile, 1·451 Å, and aniline, 1·402 Å. Although the relatively low precision of our structural determination prevents a detailed comparison, the observed structural features are on the whole consistent with the assumption about the absence of dependence on *meta* (or *para*) substitution.

The molecular structure of PCA, however, clearly shows the effects of through-conjugation, caused by the strong π donor *para* to a π acceptor. According to Domenicano, Vaciago & Coulson (1975*a*) this situation causes exceptions to the above-mentioned rule. A marked decrease in the value of α for the π acceptor may be expected. In fact α_{CN} in PCA is 119·2°, significantly lower than the corresponding values in MCA, 121·2°, and *p*-cyanoaniline hydrochloride, 121·0° (Colapietro, Domenicano, Marciante & Portalone, 1981).

The through-conjugation effects within the PCA molecule are also revealed by its quinoidal shape: the mean length of the central bonds in the benzene ring, 1·374 Å, is significantly shorter than the mean bond length of the lateral bonds, 1·401 Å, and the C–NH$_2$ and C–CN bond lengths, 1·360 and 1·430 Å respectively, are significantly shorter than the corresponding values in MCA.

The benzene ring is strictly planar in both structures (Table 3); in MCA only small deviations from the plane (the N atoms of the amino group on one side and the cyano group on the other side) are observed; PCA shows a slight bending of the substituents on the same side, out of the ring. A more important difference between the two structures lies in the position of the amino-group plane in comparison with the benzene-ring plane. Despite the high standard deviations on the positional parameters of the H atoms, it is clear that in MCA the two groups are far from being coplanar, as can also be seen from Figs. 1 and 3: Colligiani & Ambrosetti (1977) determined an angle of 33° 10′ ± 2° 30′ between the NH$_2$ group and the benzene ring, by ^{14}N NQR measurements.

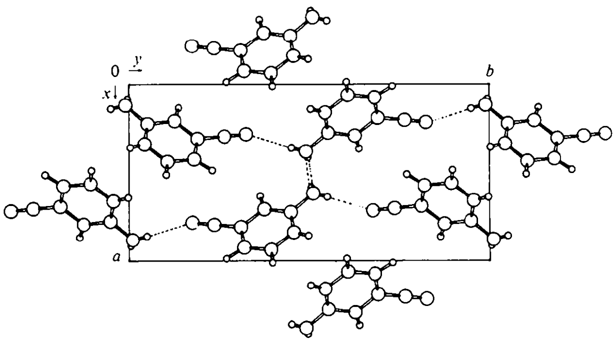

Fig. 3. *ORTEP* drawing of the MCA crystal structure projected down the [001] direction. Thermal parameters of all the atoms are spheres of arbitrary size. Intermolecular hydrogen bonds are represented by dashed lines; those ending with dots indicate that the bond is associated with a nitrogen atom translated one unit in the [001] direction.

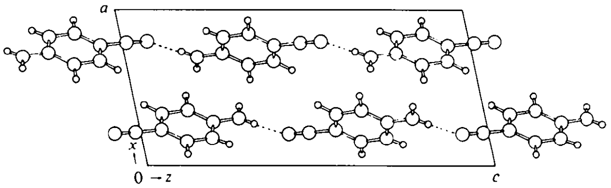

Fig. 4. *ORTEP* drawing of the PCA crystal structure projected down the [010] direction. Thermal parameters of all the atoms are spheres of arbitrary size. Intermolecular hydrogen bonds are represented by dashed lines.

In contrast, the amino group of PCA is nearly coplanar with the benzene ring (Fig. 2 and Fig. 4), which is in keeping with the observations of Colligiani & Ambrosetti (1977), who obtained a value of 12° 30′ ± 1° 30′ for the dihedral angle between the two planes.

The different angles of the NH$_2$ plane with the plane of the benzene ring in the two compounds are a further indication of a difference in conjugation: the short C–NH$_2$ bond distance in PCA corresponds to a nearly trigonal conformation of the amino group; the longer bond distance in MCA corresponds to an intermediate conformation of the amino group. The longest distance found in *p*-cyanoaniline hydrochloride (C–NH$_3^+$ 1·467 Å) (Colapietro, Domenicano, Marciante & Portalone, 1981) corresponds to a tetrahedral conformation of the NH$_3^+$ group with no conjugation at all.

The packing of the molecules in the crystals is shown in Figs. 3 and 4. In MCA it is assured by a system of hydrogen bonds involving the H atoms of the amino group and the two N atoms in each molecule: H(5) is involved in an intermolecular hydrogen bond with the lone-pair orbital of the amino group, with an N···N distance of 3·16 Å; H(6) is involved in an intermolecular hydrogen bond with the lone pair of the cyano group, with an N···N distance of 3·19 Å (Fig. 3).

In PCA only one H atom of the amino group is engaged in hydrogen bonding, with the N atom of the cyano group as acceptor and an N···N distance of 3·254 Å. In our view a second hydrogen bond is prevented in this compound by the through-conjugation which makes the lone pair in the amino group unavailable for hydrogen bonding.

The results of our structural analysis confirm the indications of ^{14}N NQR measurements, thus explaining the anomalies in the quadrupole parameters $|e^2qQ|$ and η in *m*-cyanoaniline and *p*-cyanoaniline.

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The Structures of 2-Hydroxy-5-methylbenzoic Acid and Dimorphs of 2,5-Dihydroxybenzoic Acid

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Abstract

The crystal structures of 2-hydroxy-5-methylbenzoic acid (1), $C_8H_8O_3$, and the ordered [2(*o*)] and disordered [2(*d*)] forms of 2,5-dihydroxybenzoic acid, $C_7H_6O_4$, have been determined. The crystal data are: $P2_1/a$, $a = 21{\cdot}24$ (2), $b = 5{\cdot}114$ (7), $c = 3{\cdot}307$ (9) Å, $\beta = 103{\cdot}76$ (8)°, $Z = 4$, $D_x = 1{\cdot}311$, $D_m = 1{\cdot}31$ Mg m^{-3}, m.p. 424–425·5 K for 1; $P2_1/a$, $a = 23{\cdot}945$ (2), $b = 4{\cdot}908$ (1), $c = 5{\cdot}621$ (1) Å, $\beta = 100{\cdot}981$ (8)°, $Z = 4$, $D_x = 1{\cdot}578$, $D_m = 1{\cdot}57$ Mg m^{-3}, m.p. 481–483 K for 2(*o*); and Pa, $a = 11{\cdot}229$ (2), $b = 11{\cdot}830$ (3), $c = 4{\cdot}966$ (4) Å, $\beta = 90{\cdot}50$ (3)°, $Z = 4$, $D_x = 1{\cdot}552$, $D_m = 1{\cdot}55$ Mg m^{-3}, m.p. 488–490 K for 2(*d*). The final R values for 1, 2(*o*) and 2(*d*) were 0·073, 0·035 and 0·039 for 904, 961 and 960 non-zero reflexions, respectively. Molecules of 2 show a quinonoid structure as found in salicylic acid. The crystal structures of 1 and 2(*o*) are of the benzoic acid type, and that of 2(*d*) is of the salicylic acid type. The crystal structures of 1, 2(*o*) and 2(*d*) are mainly determined by van der Waals interactions between the acid dimers, and the hydrogen bonding of the phenolic hydroxylic groups plays only an additional role. The morphotropism of benzoic acids is discussed.

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Introduction

The present work on benzoic acids forms part of a systematization of the crystal structures of aromatic compounds (Haisa, 1978). The crystal structures of monocarboxylic acids have recently been discussed on the basis of morphotropism (Kashino & Haisa, 1980). The crystal structures of the title compounds have been examined in order to see the effects on them of the phenolic hydroxylic groups.