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Structure and Crystal Packing of 4-Aminobenzonitriles and 4-Amino-3,5-dimethylbenzonitriles at Various Temperatures

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Abstract

The amino N atom in 4-aminobenzonitrile (ABN) and 4-(dimethylamino)benzonitrile (DMABN) has a pyramidal character, with values of 34 (3) and 11.9 (3)°, respectively, for the angle between the planes of the amino group and the phenyl ring. In 3,5-dimethyl-4-(dimethylamino)benzonitrile (MMD) at 173 K, the dimethylamino group is twisted over an angle of 59.3 (2)° with respect to the phenyl plane. In addition, the amino N(1) atom is not located in the plane of the phenyl ring, with an

out-of-plane displacement of 0.117 (5) Å. The N–phenyl bond length in MMD of 1.414 (3) Å is larger that that in the four other aminobenzonitriles, for which an average bond length of 1.367 Å is found. With DMABN, the crystal structure consists of stacks with an alternating orientation of the molecules. In the crystals of ABN, 3,5-dimethyl-4-(methylamino)benzonitrile (MHD) and 4-amino-3,5-dimethylbenzonitrile (HHD), hydrogen bonding is an important structural element. In ABN and MHD, hydrogen bonds are formed between an amino H atom and the cyano N atom of adjacent molecules. In HHD, each H atom is linked to a cyano N atom of two different neighbouring molecules, in a layered structure consisting of squares and octagons. Temperature-dependent solid–solid phase transitions are observed with all five aminobenzonitriles studied here. Crystals of the low-temperature phase could only be obtained from ABN, with lattice constants which are considerably different from those observed at room temperature.

Introduction

The photophysical behaviour in dilute solution of the donor-/acceptor-substituted benzene derivative 4-(dimethylamino)benzonitrile (DMABN) in the excited singlet state has attracted considerable attention since the discovery of its dual fluorescence by Lippert (Lippert et al., 1961; Lippert, Lüder & Boos, 1962). In brief, the dual fluorescence originates from two excited state species, the initially excited (LE) state and a charge-transfer (CT) state with a considerably larger dipole moment (Baumann et al., 1992; Schuddeboom et al., 1992). This CT state cannot be prepared by direct absorption from the ground state, but is produced from the LE state via an intramolecular charge-transfer (ICT) reaction on a picosecond time scale (Leinhos, Kühnle & Zachariasse, 1991).
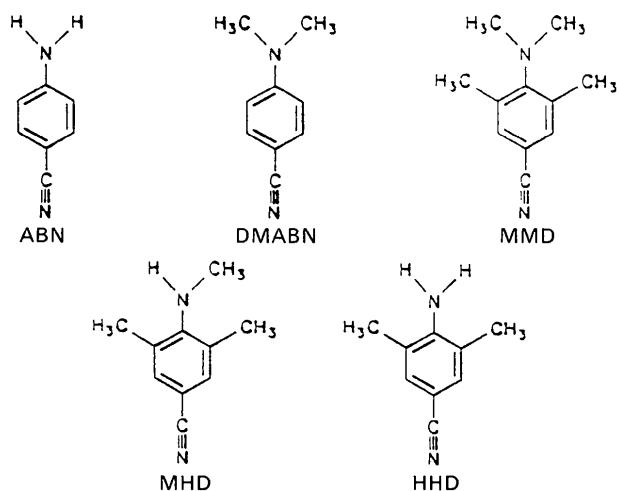
For the explanation of this unusual dual fluorescence a surprisingly large variety of mechanisms has been presented in the literature (Grabowski, Rotkiewicz, Siemiarczuk, Cowley & Baumann, 1979; Rettig, 1986). Among these mechanisms, the model of 'twisted internal charge transfer' (TICT) pioneered by Grabowski (Rotkiewicz, Grellmann & Grabowski, 1973) occupies a predominant place. This model ascribes the CT state of molecules such as DMABN to originating from the supposedly planar LE state by a rotation around the N–phenyl bond, leading to a rotational isomer in which the plane of the phenyl ring is perpendicular to that of the amino group. With 3,5-dimethyl-4-(dimethylamino)benzonitrile (MMD), a molecule in which the dimethylamino group is forced toward a perpendicular configuration by two ortho-methyl substituents, only CT fluorescence could be detected (Rotkiewicz, Grabowski, Króowczyónski & Kühnle, 1976). This was considered to be support for the TICT mechanism. It has recently been shown, however, that MMD is in fact dual fluorescent on a picosecond time scale (Zachariasse, von der Haar, Hebecker, Leinhos & Kühnle, 1993).

As an alternative mechanism, it has been postulated recently (Zachariasse, von der Haar, Hebecker, Leinhos & Kühnle, 1993) that ICT in DMABN and related molecules occurs as a consequence of solvent-induced pseudo-Jahn–Teller coupling between the two lowest singlet excited states S_1 and S_2(CT). This S_2(CT) state is similar to the valence-bond CT state in donor-substituted benzenes such as aniline (Murrell, 1963; Majumdar, Sen, Bhattacharyya & Bhattacharyya, 1991).

For a further elucidation of the structural changes accompanying and governing the excited-state ICT processes in molecules such as DMABN and MMD, a knowledge of the molecular structure in the ground state is important. We report here on the crystal structure, measured in some cases at a series of temperatures, of DMABN and ABN, as well as of the three related compounds MMD, MHD and HHD. Interest is focused on (a) the pyramidal character (sp^2/sp^3) of the amino N atom, (b) the twist angle around the phenyl/amino bond, with respect to the phenyl ring, and (c) the bond length changes in the various compounds. In addition, the different crystal packings and temperature-dependent phase transitions observed with the five molecules are presented.

Experimental

Crystals of all the compounds, except ABN, were obtained from cyclopentane solution at 255 K. The low-temperature phase of ABN (see below) was crystallized at 255 K from tetrahydrofuran. The crystal-

Table 1. *Crystal data and structure refinement*

	ABN	DMABN	DMABN	MMD	MHD	MHD	MHD	MHD	MHD	HHD
Formula	$C_7H_6N_2$	$C_9H_{10}N_2$	$C_9H_{10}N_2$	$C_{11}H_{14}N_2$	$C_{10}H_{12}N_2$	$C_{10}H_{12}N_2$	$C_{10}H_{12}N_2$	$C_{10}H_{12}N_2$	$C_{10}H_{12}N_2$	$C_9H_{10}N_2$
M_r	118.1	146.2	146.2	174.2	160.2	160.2	160.2	160.2	160.2	146.2
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P4_32_12$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/c$
Z	4	4	4	4	4	4	4	4	4	16
Temperature (K)	153 (2)	293 (2)	253 (2)	173 (2)	293 (2)	233 (2)	193 (2)	173 (2)	153 (2)	188 (2)
a (Å)	5.753 (2)	6.304 (2)	6.325 (2)	7.737 (2)	7.482 (2)	7.466 (2)	7.467 (2)	7.467 (2)	7.468 (2)	17.100 (2)
b (Å)	7.503 (2)	7.937 (2)	7.917 (2)	7.737 (2)	7.990 (2)	7.906 (2)	7.862 (2)	7.842 (2)	7.821 (2)	22.385 (2)
c (Å)	14.270 (2)	17.203 (2)	17.026 (3)	16.594 (3)	15.322 (2)	15.251 (2)	15.218 (2)	15.203 (2)	15.187 (2)	8.747 (2)
β (°)	90	91.59 (2)	90.95 (2)	90	92.51 (2)	92.37 (2)	92.18 (2)	92.06 (2)	91.02 (2)	98.99 (2)
V (Å³)	616.0 (2)	860.4 (2)	852.5 (2)	993.3 (3)	915.1 (2)	899.4 (2)	892.7 (2)	889.7 (2)	886.9 (2)	3307.1 (6)
$F(000)$	248	312	312	376	344	344	344	344	344	1248
μ (mm⁻¹)	0.08	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
D_x (g cm⁻³)	1.274	1.129	1.139	1.165	1.163	1.183	1.192	1.196	1.200	1.174
Crystal dimensions (mm)	0.9×0.8×0.4	0.6×0.5×0.4	0.8×0.6×0.5	0.6×0.5×0.4	0.6×0.4×0.3	0.7×0.7×0.5	0.7×0.7×0.5	0.8×0.7×0.6	0.8×0.8×0.7	0.5×0.4×0.3
Reflections collected	1248	1292	1132	2006	6545	1986	2272	2276	2033	4320
Independent reflections	1061	1118	1113	1445	1615	1593	1584	1582	1578	2155
Reflections used	1061	1195	1095	1445	1615	1593	1584	1582	1577	2154
Range of h, k, l	$-2 \le h \le 7$ $-9 \le k \le 9$ $-18 \le l \le 18$	$-7 \le h \le 6$ $-6 \le k \le 9$ $-16 \le l \le 21$	$-7 \le h \le 7$ $-3 \le k \le 9$ $-12 \le l \le 20$	$-1 \le h \le 10$ $-10 \le k \le 10$ $-23 \le l \le 23$	$-8 \le h \le 8$ $-9 \le k \le 9$ $-18 \le l \le 18$	$-8 \le h \le 8$ $-8 \le k < 9$ $-17 \le l \le 18$	$-8 \le h \le 8$ $-9 \le k \le 9$ $-18 \le l \le 18$	$-8 \le h \le 8$ $-9 \le k \le 9$ $-18 \le l \le 18$	$-8 \le h \le 8$ $-8 \le k \le 9$ $-17 \le l \le 18$	$-18 \le h \le 18$ $-24 \le k \le 24$ $-2 \le l \le 9$
$2\theta_{max}$ (°)	55	45	45	60	50	50	50	50	50	45
R_1 [for $F > 4\sigma(F)$]	0.0444	0.0431	0.0482	0.0421	0.0643	0.0523	0.0439	0.0422	0.0500	0.0587
wR_2 (for all data)	0.1216	0.1279	0.1586	0.1288	0.1720	0.1387	0.1210	0.1179	0.1237	0.1587
g_1	0.0905	0.0455	0.0542	0.0787	0.0803	0.0537	0.0541	0.0561	0.0478	0.0988
g_2	0.0406	0.1209	0.1931	0.0920	0.1678	0.3532	0.2910	0.2812	0.2792	0.0
S	1.025	1.078	1.074	1.101	1.031	1.029	1.040	1.041	1.046	1.037
Max. LS shift/e.s.d	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
No. of parameters	89	103	103	69	117	117	117	117	117	221
Residual peak (e Å⁻³)	0.23	0.07	0.09	0.23	0.18	0.17	0.18	0.16	0.16	0.46
Extinction coefficient	—	0.024 (5)	0.020 (5)	0.032 (9)	0.032 (9)	0.022 (5)	0.28 (5)	0.021 (5)	0.016 (4)	—

lographic data are summarized in Table 1.* The intensities were measured on a Siemens Stoe-AED diffractometer using graphite-monochromated Mo $K\alpha$ radiation (0.71073 Å) and the profile-fitting mode involving variable scan width and speed (Clegg, 1981). The cell constants were determined by fitting a number of reflections in the range $20 \le 2\theta \le 25°$ [(ABN) 56, (DMABN) 60, (MMD) 64, (MHD) 56, (HHD) 57]. The repeated measurement of three standard reflections revealed no appreciable decay during the course of any of the data collections.

The structures were solved by direct methods with *SHELXS*-90 (Sheldrick, 1990). Atomic scattering factors were taken from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). All atoms other than hydrogen were refined

anisotropically (Sheldrick, 1992). For the H atoms bound to C atoms, the riding model was used. The U values were fixed. The positions of the H atoms bound to N atoms and the U values for all of these H atoms were refined freely.

With ABN, DMABN and MHD, one molecule is present in the asymmetric unit, with MMD half a molecule and with HHD two half molecules and a whole molecule make up the asymmetric unit. A twofold axis generates the whole molecule out of the halves where half molecules are present.

In the crystal of HHD, the four, and in ABN the two, independent N—H distances were restrained to be equal. The structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g1P)^2 + g2P$, with $P = (F_o^2 + 2F_c^2)/3$. For the structures of DMABN, MMD and MHD, a secondary extinction coefficient χ was applied [$F_c^* = kF_c(1 + 0.001\chi F_c^2 \lambda^3/ \sin 2\theta)^{-1/4}$, with k = overall scale factor].

The atomic coordinates for all the structures discussed here are given in Tables 2–6. In all the figures, the anisotropic displacement parameters are depicted

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* Lists of structure factors and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71499 (299 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE0122]

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($\mathring{A}^2 \times 10^3$) *for ABN at* 153 K

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
N(1)	7474 (3)	3765 (2)	5925 (1)	30 (1)
C(1)	6067 (3)	4453 (2)	5240 (1)	23 (1)
C(2)	3881 (3)	5165 (2)	5473 (1)	24 (1)
C(3)	2508 (3)	5922 (2)	4801 (1)	24 (1)
C(4)	3246 (4)	5985 (2)	3866 (1)	25 (1)
C(5)	5405 (4)	5268 (2)	3628 (1)	26 (1)
C(6)	6789 (4)	4505 (2)	4300 (1)	26 (1)
C(7)	1788 (4)	6746 (3)	3160 (1)	28 (1)
N(2)	606 (4)	7347 (2)	2594 (1)	38 (1)

Table 3. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($\mathring{A}^2 \times 10^3$) *for DMABN at* 253 K

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	1970 (4)	1584 (3)	7148 (2)	75 (1)
C(2)	1289 (4)	793 (3)	7837 (2)	80 (1)
C(3)	2467 (5)	857 (3)	8519 (2)	85 (1)
C(4)	4366 (5)	1728 (3)	8556 (2)	84 (1)
C(5)	5052 (5)	2515 (3)	7876 (2)	94 (1)
C(6)	3890 (5)	2451 (3)	7191 (2)	91 (1)
N(1)	812 (4)	1528 (3)	6465 (2)	90 (1)
C(7)	1672 (5)	2191 (5)	5740 (2)	122 (1)
C(8)	-1043 (4)	484 (4)	6388 (2)	103 (1)
N(2)	6686 (5)	1878 (4)	9808 (2)	136 (1)
C(9)	5622 (6)	1795 (4)	9259 (3)	105 (1)

at the 50% probability level. Selected bond lengths and angles are listed in Table 7. For the structures DMABN and MHD, data sets at several temperatures were collected. A modified Siemens LT2 cooling device was used. When average values of crystal data are quoted in the subsequent discussion, they refer to the following temperatures: ABN, 153 K; DMABN, 253 K; MMD, 173 K; MHD, 173 K; HHD, 188 K.

Temperature of phase transitions

With all the molecular crystals studied in this paper, a solid–solid phase transition occurs upon lowering the temperature. For the temperatures at which these transitions occur, the following values are found by looking at the broadening of the profiles while lowering the temperature: DMABN (between 253 and 233 K), MMD (between 173 and 153 K), MHD (at around 148 K) and HHD (at around 173 K). In the case of ABN, the phase transition occurs above 255 K, the temperature at which the crystals were grown, and below 293 K, where the high-temperature phase was investigated (Merlino & Sartori, 1982). The structure determination of MHD at 153 K is less precise than that at 173 K, as the former data were determined close to

Table 4. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($\mathring{A}^2 \times 10^3$) *for MMD at* 173 K

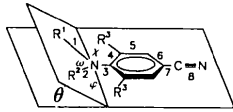U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(4)	3589 (2)	5217 (2)	484 (1)	28 (1)
C(3)	2316 (2)	3964 (2)	494 (1)	26 (1)
C(5)	5039 (2)	5039 (2)	0	29 (1)
C(7)	6341 (2)	6341 (2)	0	37 (1)
C(2)	2495 (2)	2495 (2)	0	26 (1)
C(6)	819 (2)	4178 (2)	1060 (1)	37 (1)
C(1)	1624 (2)	-527 (2)	200 (1)	40 (1)
N(2)	7390 (2)	7390 (2)	0	55 (1)
N(1)	1263 (5)	1172 (5)	-122 (2)	30 (1)

Table 5. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($\mathring{A}^2 \times 10^3$) *for MHD at* 173 K

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
N(1)	1429 (2)	5968 (2)	3198 (1)	46 (1)
N(2)	-3777 (2)	9608 (2)	6192 (1)	53 (1)
C(1)	3277 (3)	5645 (4)	3181 (1)	95 (1)
C(2)	466 (2)	6776 (2)	3823 (1)	34 (1)
C(3)	1055 (2)	6953 (2)	4711 (1)	35 (1)
C(4)	2832 (2)	6305 (2)	5074 (1)	50 (1)
C(5)	-64 (2)	7711 (2)	5291 (1)	37 (1)
C(6)	-1745 (2)	8328 (2)	5034 (1)	37 (1)
C(7)	-2874 (2)	9059 (2)	5668 (1)	42 (1)
C(8)	-2308 (2)	8180 (2)	4160 (1)	36 (1)
C(9)	-1247 (2)	7417 (2)	3557 (1)	35 (1)
C(10)	-1913 (2)	7253 (2)	2618 (1)	45 (1)

Table 6. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($\mathring{A}^2 \times 10^3$) *for HHD at* 188 K

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
N(1)	3916 (1)	3154 (1)	5574 (3)	35 (1)
C(1)	3342 (1)	3158 (1)	4307 (3)	30 (1)
C(2)	3083 (1)	2615 (1)	3573 (3)	28 (1)
C(3)	2479 (1)	2627 (1)	2332 (3)	29 (1)
C(4)	2128 (2)	3167 (1)	1762 (3)	28 (1)
C(5)	2409 (2)	3698 (1)	2485 (3)	31 (1)
C(6)	2999 (1)	3706 (1)	3735 (3)	28 (1)
C(7)	3452 (2)	2038 (1)	4163 (3)	35 (1)
C(8)	3287 (2)	4277 (1)	4511 (3)	40 (1)
C(9)	1517 (2)	3176 (1)	476 (3)	34 (1)
N(2)	1016 (2)	3193 (1)	-576 (3)	43 (1)
N(3)	5000	7157 (1)	7500	34 (1)
C(10)	5000	6548 (2)	7500	28 (1)
C(11)	4504 (1)	6234 (1)	6324 (3)	27 (1)
C(12)	4513 (2)	5621 (1)	6356 (3)	30 (1)
C(13)	5000	5302 (2)	7500	27 (1)
C(14)	3979 (2)	6571 (1)	5098 (3)	36 (1)
C(15)	5000	4670 (2)	7500	32 (1)
N(4)	5000	4154 (2)	7500	43 (1)
N(5)	5000	-811 (1)	7500	41 (1)
C(16)	5000	-201 (2)	7500	31 (1)
C(17)	5581 (1)	113 (1)	8522 (3)	28 (1)
C(18)	5562 (2)	728 (1)	8504 (3)	33 (1)
C(19)	5000	1045 (2)	7500	28 (1)
C(20)	6196 (2)	-224 (1)	9585 (3)	38 (1)
C(21)	5000	1679 (2)	7500	34 (1)
N(6)	5000	2194 (2)	7500	43 (1)

Table 7. Comparison of main structural features of five aminobenzonitriles at various temperatures

	T (K)	1	2	3	4ᵃ	5ᵃ	6ᵃ	7	8	ω	χ	φ	θ	N out of planeᵇ	N···Nᶜ
ABN	153	0.90(2)	0.90(2)	1.370(3)	1.405(3)	1.369(3)	1.398(3)	1.431(3)	1.148(3)	114(2)	115(2)	117(2)	34(3)	0.059(3)	3.083(3)
DMABN	293	1.440(3)	1.457(3)	1.367(3)	1.396(3)	1.368(3)	1.381(3)	1.434(4)	1.145(3)	116.5(2)	121.6(2)	120.7(2)	10.8(2)	0.011(4)	–
	253	1.439(3)	1.456(3)	1.365(3)	1.400(4)	1.370(4)	1.388(4)	1.427(5)	1.145(4)	116.4(3)	121.5(2)	120.6(3)	11.9(3)	0.005(4)	–
MMD	173	1.447(5)	1.434(5)	1.414(3)	1.408(2)	1.382(2)	1.387(2)	1.425(3)	1.147(3)	116.2(2)	118.3(3)	119.2(3)	59.3(2)	0.117(5)	–
		1.425(2)ᵈ		1.398(2)ᵈ	1.408(2)ᵈ	1.380(2)ᵈ	1.386(2)ᵈ	1.427(3)ᵈ	1.148(3)ᵈ	118.1(2)ᵈ	120.94(9)ᵈ		57.90(5)ᵈ	0.0ᵈ	
MHD	293	0.89(3)	1.479(4)ʳ	1.369(3)	1.414(3)	1.371(3)	1.383(3)	1.430(4)	1.141(3)	115(2)	112(2)	130.4(3)	14.9(9)	0.058(4)	3.127(4)
	233	0.86(2)	1.465(3)ʳ	1.370(3)	1.411(3)	1.373(3)	1.384(3)	1.423(3)	1.144(3)	114(2)	113(2)	130.2(3)	16.3(8)	0.058(4)	3.101(3)
	193	0.89(2)	1.458(2)ʳ	1.367(2)	1.415(2)	1.370(2)	1.385(2)	1.425(2)	1.146(2)	113(2)	113(2)	129.8(2)	16.6(6)	0.061(2)	3.087(2)
	173	0.89(2)	1.455(2)ʳ	1.368(2)	1.416(2)	1.371(2)	1.387(2)	1.423(2)	1.146(2)	113(2)	113(2)	129.6(2)	17.1(6)	0.066(2)	3.081(2)
	153	0.91(2)	1.458(3)ʳ	1.360(3)	1.422(3)	1.368(3)	1.390(3)	1.418(3)	1.139(3)	112(2)	115(2)	129.2(2)	15.8(8)	0.068(3)	3.080(3)
HHD	188	0.93(2)ᵍ	0.93(2)ᵍ	1.364(5)ᵍ	1.415(3)ᵍ	1.374(4)ᵍ	1.397(3)ᵍ	1.414(6)ᵍ	1.154(5)ᵍ	120(2)ᵍ	120(2)ᵍ	118(3)ᵍ	12(4)ᵍ	0.053(4)ᵍ	3.180(3)ᵍ
													3(3)ʰ	0.0ʰ	
													2(3)ʰ	0.0ʰ	

Notes: (a) Average of equivalent bond distances. (b) Least-squares plane of the six ring C atoms. (c) Distance between N atoms involved in a hydrogen bridge. (d) Values of the refinement with N(1) fixed on the twofold axis. (e) Libration-corrected distances, C riding on N (Johnson, 1970). (f) Average of equivalent molecules. (g) Values of the whole molecule in the asymmetric unit. (h) Values of the two molecules at the twofold axis.

the phase-transition temperature, resulting in considerable broadening of all profiles.

Large amplitude motion in MMD and MHD

Two different sets of structural parameters are quoted for MMD in Table 7. The first set refers to a refinement with the amino N atom N(1) positioned on the twofold axis. However, the relatively high expansion of the anisotropic displacement parameter of N(1) perpendicular to the plane defined by the three neighbouring atoms in this refinement means that a disorder or a large amplitude vibration is present in the crystal structure (see Fig. 4, below). In order to model the disorder, the N atom was refined in a general position rather than being fixed on the twofold axis. The distance between N(1) and N(1a) is 0.417 (7) Å. All the structural parameters of MMD quoted in the following discussion refer to the latter refinement. The data resulting from both refinements are presented in Table 7.
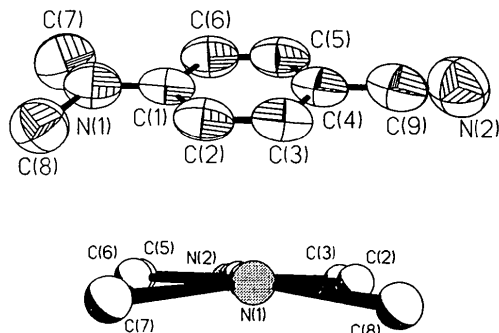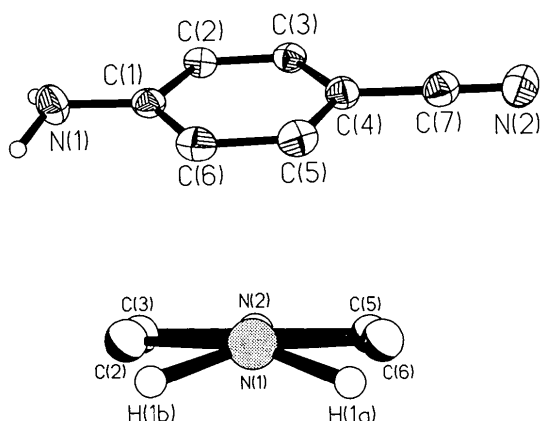
Fig. 1. Molecular structure of 4-(dimethylamino)benzonitrile (DMABN) at 253 K. The lower part of the figure is a view along the long molecular axis. Note the out-of-plane position of the amino methyl groups, C(7) and C(8), see Table 7.

The anisotropic displacement parameter of the amino C atom C(1) in MHD indicates the presence of a considerable libration of the methyl group connected to the N atom. Hence, the distances given in Table 7 are corrected for libration (Johnson, 1970), resulting in an increase of the bond distance from 0.12 Å for the room-temperature data set to 0.19 Å for the data at 153 K.

Results and discussion

The numbering of the various bonds and angles in the aminobenzonitriles studied here is given in the diagram incorporated in Table 7.

Pyramidal character of the amino N atom and twist angle

The solid-state structure of DMABN in the crystal at 253 K is depicted in Fig. 1.

An interesting feature of this structure (Table 7) is the finding that the dimethylamino group in DMABN is not coplanar with the phenyl ring: the amino group has considerable pyramidal character. The inversion angle θ (defined in Table 7) between the plane through the three atoms C(7), N(1) and C(8) of the dimethylamino group and that of the phenyl ring amounts to 10.8 (2)° at 293 K and 11.9 (3)° at 253 K. The distances from the atoms C(7) and C(8) to the phenyl plane are the same [0.156 (5) and 0.148 (5) Å at 253 K]. An even more pronounced pyramidal configuration of the amino N atom N(1) is observed with ABN, for which in the low-temperature phase at 153 K (Figs. 2 and 3) an inversion angle θ of 34 (3)° is observed (Table 7). At 293 K, in the high-temperature phase (see below), a considerably smaller angle θ of 7.5° is found (Merlino & Sartori, 1982). In ABN, the amino H

atoms H(1*a*) and H(1*b*) have the same distance to the plane of the phenyl ring [0.21 (3) and 0.21 (3) Å at 153 K].

For the out-of-plane distance of the amino H atom H(1) and the amino C atom C(1) of MHD, average values of 0.042 and 0.283 Å, respectively, are obtained between 293 and 173 K. The data for MHD at 153 K are not included in this comparison. The structure determination of MHD at this temperature is less precise than that at 173 K, see the e.s.d. values in Table 7, as the former data were determined close to the phase-transition temperature. In HHD, for the whole molecule present in the asymmetric unit, the inversion angle θ is equal to 12 (4)°, slightly smaller than in MHD, see Table 7 and Fig. 3. Also in MMD, the N(1) atom has a

Fig. 2. Molecular structure of 4-aminobenzonitrile (ABN) at 153 K. The lower part of the figure is a view along the long molecular axis. The amino H(1*a*) and H(1*b*) atoms are in an out-of-plane position with respect to the phenyl ring, see Table 7.
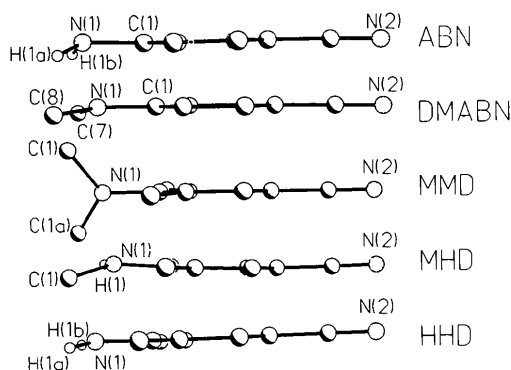
Fig. 3. Molecular structures (side-on views) of 4-aminobenzonitrile (ABN) at 153 K, 4-(dimethylamino)benzonitrile (DMABN) at 253 K, 3,5-dimethyl-4-(dimethylamino)benzonitrile (MMD) at 173 K, 3,5-dimethyl-4-(methylamino)benzonitrile (MHD) at 173 K and 4-amino-3,5-dimethylbenzonitrile (HHD) at 188 K. Note the pyramidal character of the amino N(1) atom in ABN and DMABN, and the pronounced twist angle of 59.3 (2) (Table 7) in MMD.

pronounced pyramidal character, as will be shown in the next section.

The inversion angle θ of 34° between the phenyl and amino planes in the case of crystalline ABN at 153 K approaches the values 37° and 42°, determined for aniline vapour by microwave spectroscopy (Lister, Tyler, Høg & Wessel Larsen, 1974) and by resonance fluorescence experiments (Quack & Stockburger, 1972), respectively. Similar results have been obtained for *N,N*-dimethylaniline, with an inversion angle of 27° between the planes of the ring and the dimethylamino group (Cervellati, Dal Borgo & Lister, 1982). The inversion angle θ of 15°, determined for gas-phase DMABN *via* microwave spectroscopy experiments (Kajimoto, Yokoyama, Ooshima & Endo, 1991), is somewhat larger than the angle of 12° found here for crystalline DMABN at 253 K.

The sum of the angles ω, χ and φ around the amino N atom N(1) is in accordance with the pyramidal character of N(1) in the present amino-benzonitriles. In ABN, this sum equals 346° at 153 K (Table 7), a value between that for a completely pyramidal N(sp^3) atom (329°) and that for a completely planar N(sp^2) atom (360°).

With MHD, the sum of the angles around N(1) decreases with temperature from 357.4° at 293 K to 356.2° at 153 K, parallel with the increase in the inversion angle θ from 14.9 to 17.1° (Table 7). In the case of MMD, finally, the N(1) angles sum to 353.8°, which points to a pronounced pyramidal character for the amino N atoms, see Table 7.

Out-of-plane displacement of the amino N atom

The amino N atom N(1) of DMABN can be considered to be located in the plane defined by the phenyl ring, in view of its out-of-plane distance of only 0.011 (4) Å at 293 K and 0.005 (4) Å at 253 K (Table 7). For ABN, a somewhat larger vertical displacement for N(1) of 0.059 (3) Å at 153 K is observed (0.023 Å at 293 K).

In contrast to DMABN, the amino N atom of MMD is not located in the plane of the phenyl ring (Fig. 4): an out-of-plane distance of 0.117 (5) Å (173 K, Table 7) is observed.

This displacement of N(1) is considerably larger than that found with ABN (see above) and also larger than the out-of-plane distances of N(1) in MHD and HHD. For MHD a distance of 0.066 (2) Å (173 K) is observed, whereas for HHD the N atom N(1) is close to the phenyl plane: 0.018 (4) Å (188 K). Examples of out-of-plane distances of N(1) reported for other aromatic amines are: 0.060 Å for 3-aminobenzonitrile (Merlino & Sartori, 1982) and 0.022 Å for 4-nitroaniline (Trueblood, Goldish & Donohue, 1961).

Twist angle and molecular structure for MMD, MHD and HHD

The most prominent feature of the molecular structure of MMD is the magnitude of the angle θ [59.3 (2)^c at 173 K], see Fig. 4 and Table 7. This twist is caused by the steric requirements of the two amino methyl substituents which are hindered by the two *ortho*-methyl groups on the phenyl ring. In MHD (Fig. 5), where only one methyl substituent is present
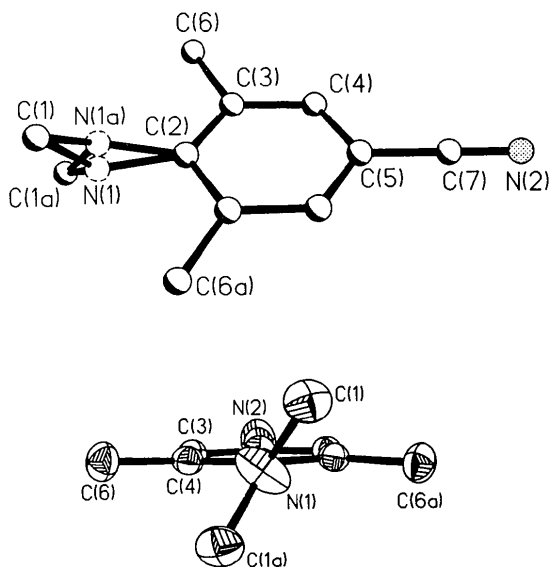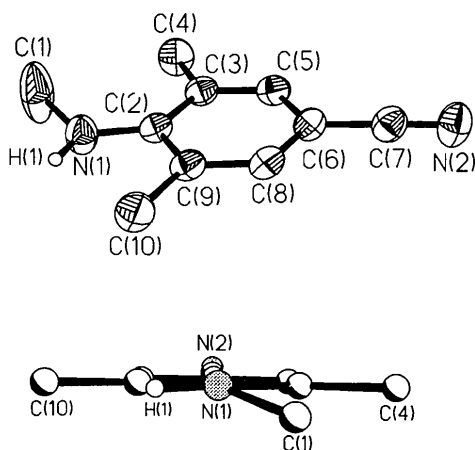

Fig. 4. Molecular structure of 3,5-dimethyl-4-(dimethylamino)-benzonitrile (MMD) at 173 K. The lower part of the figure is a view along the long molecular axis, showing the pronounced twist angle of the dimethylamino group. The anisotropic displacement parameter of the amino N(1) atom indicates a disorder in the crystal structure or a large amplitude vibration, see text.

in the amino group, the steric influence of the two *ortho*-methyl groups is strongly reduced compared with MMD, as can be seen from the clearly smaller angle θ of the N—CH₃ bond [17.1 (6)^c at 173 K, Table 7] between the plane through the atoms C(1), N(1) and C(2) and that of the phenyl ring.

An inversion angle θ of 12 (4)^c at 188 K is found in HHD (Fig. 6 and Table 7). The out-of-plane distances of the amino H atoms H(1a) and H(1b) are not strongly different [0.07 (3) and 0.01 (3) Å] considering the e.s.d. values. This shows that the twist angle between the planes of the amino group and the phenyl ring is close to zero, similar to that found with ABN and DMABN (see above). These results indicate that the NH₂ group in HHD is only slightly hindered by the two *ortho*-methyl substituents. The amino N atom N(1) has an out-of-plane distance of 0.053 (4) Å.

In summary, the effect of the steric hindrance between the *ortho*-methyl groups on the phenyl ring and the dimethylamino group in MMD is apparently twofold: a rotation around the dimethylamino/phenyl bond as well as a displacement of the N(1) atom, as discussed above. Both structural disturbances are partially relieved by the replacement of the amino methyl groups by H atoms.

N–phenyl bond length increase in MMD

The N–phenyl bond length of 1.414 (3) Å in MMD is considerably larger than that in the two other 4-amino-3,5-dimethylbenzonitriles, for which values of 1.368 (2) Å (MHD, 173 K) and 1.364 (5) Å (HHD, 188 K) are observed, and also larger than the N–phenyl bond lengths determined here for DMABN [1.365 (3) Å, 253 K] and ABN [1.370 (3),

Fig. 5. Molecular structure of 3,5-dimethyl-4-(methylamino)-benzonitrile (MHD) at 173 K. The lower part of the figure is a view along the long molecular axis, revealing the large inversion angle (see Table 7) of the amino methyl group C(1). The H(1) atom is practically coplanar with the phenyl ring.
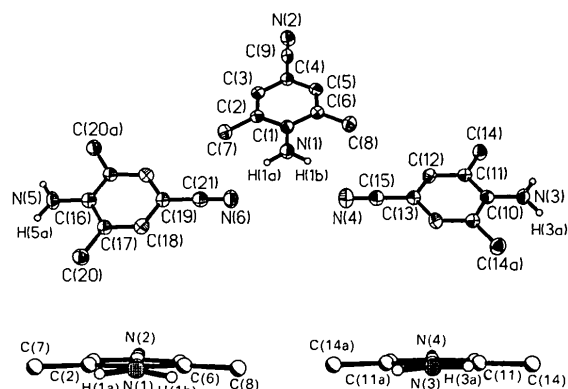

Fig. 6. Upper part: Molecular structure of the 4-amino-3,5-dimethylbenzonitrile (HHD) molecules in the asymmetric unit at 188 K. Note the out-of-plane position of the amino H atoms, see Table 7. Lower left part: view along the long molecular axis of the HHD molecule present as a whole in the asymmetric unit. Lower right part: view along the long molecular axis of one of the two HHD molecules on the twofold axis of the asymmetric unit.

153 K], see Table 7. The length of bond 3 in the latter four molecules is similar to the literature values reported for this bond in acceptor-substituted aromatic amines such as 4-nitroaniline, 1.371 Å (Trueblood, Goldish & Donohue, 1961), and 4-nitroso-N,N-diethylaniline, 1.358 Å (Talberg, 1977).

The increase in length of the N–phenyl bond of MMD by ca 0.05 Å, in comparison to the average length of this bond in ABN, DMABN, MHD and HHD (1.367 Å, Table 7), points to a decrease in the electronic coupling between the amino group and the phenyl ring in MMD, as compared with the latter four molecules. The N–phenyl bond length in MMD lies towards the value of 1.467 (2) Å measured in 4-aminobenzonitrile hydrochloride crystals (Cola-pietro, Domenicano, Marciante & Portalone, 1981), which can be considered to be a pure single bond. It is of interest to note that this latter bond length is similar to that (1.453 Å) found in the aliphatic trimethylamine (Blake, Ebsworth & Welch, 1984; Julian & Gibbs, 1988).

The more pronounced single-bond character of bond 3 in MMD, as compared with the four other aminobenzonitriles, indicates that the extent of delocalization of the nitrogen lone pair into the aromatic ring is reduced. This is due to the large deviation from planarity observed in this molecule, caused by the twist around the N–phenyl bond over an angle of 59.3 (2)° and, in addition, by the out-of-plane displacement of the N(1) atom. The gradual decrease of the steric requirements on the amino group in the series MMD, MHD and HHD, as discussed above, then again increases the amino/phenyl electronic coupling, and hence the double-bond nature of the N–phenyl bond.

The double-bond character of the N–phenyl bond in the aminobenzonitriles can formally be explained in a valence-bond (VB) approach, by taking into account the three basically planar ionic resonance structures (III)–(V) next to the two uncharged, possibly pyramidal (Lister, Tyler, Høg & Wessel Larsen, 1974) structures (I) and (II) (Fig. 7). It is seen that a double bond appears for bond 3 in the three ionic structures. A partial double bond would be expected to enhance the planarity of the aminobenzonitriles and lead to an increase in the height of the rotational barrier of the N–phenyl bond.

Quinoidal structure of the phenyl ring

Bonds 4, 5 and 6 in the phenyl ring of the five aminobenzonitriles treated in this paper are not of equal length (Table 7). In DMABN at 253 K, as an example, the bond lengths are 1.400 (4) (bond 4), 1.370 (4) (bond 5) and 1.388 (4) Å (bond 6). With ABN, MHD and HHD, the length of bond 4 is likewise clearly longer than that of the two other

bonds, of which bond 5 has the smallest length. The average values for the four molecules are 1.409 (bond 4), 1.371 (bond 5) and 1.393 Å (bond 6). This means that the aromatic ring adopts a quinoidal structure.

This deviation from sixfold symmetry in the phenyl ring is seen to be smaller in MMD, showing that also with respect to the shape of the aromatic ring this molecule is different from the four other molecules. In MMD at 173 K, bonds 5 [1.382 (2) Å] and 6 [1.387 (2) Å] have approximately the same length, whereas bond 4 is again clearly longer [1.408 (2) Å] than the two other bonds. The less pronounced quinoidal perturbation of the phenyl ring in MMD is a consequence of the reduced electronic coupling between the amino group and the phenyl ring, as discussed in the previous section.

On the basis of the VB resonance structures introduced in the previous section, it can be deduced that the central bond 5 should be shorter than the other phenyl bonds, as it appears as a double bond in three of the five VB structures. Bond 4 is a double bond in only one structure, whereas for bond 6 such a bond is present in two VB structures. This would explain the finding, generally observed in aminobenzonitriles (Merlino & Sartori, 1982), that bond 4 is longer than bond 6, which in its turn is longer than bond 5.

Amino bond angles

The bond angle ω between the methyl substituents in DMABN is 116.4 (3)° (253 K), whereas in MMD a value of 116.2 (2)° at 173 K is found. These data are in agreement with results from microwave spec-
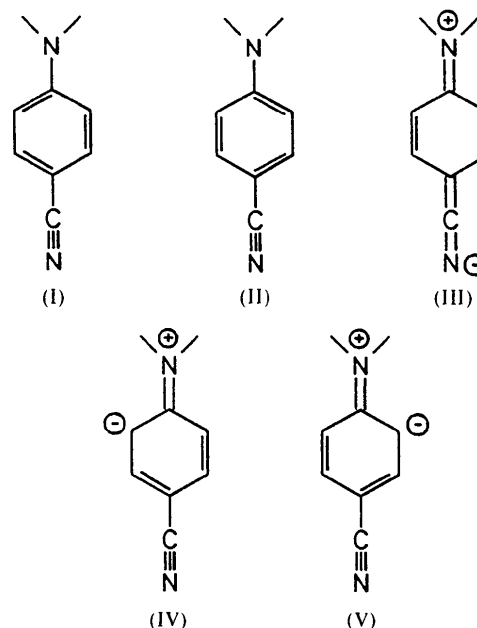

Fig. 7. Neutral and ionic resonance structures for 4-aminobenzonitrile.

troscopy experiments on DMABN, where an angle ω of 115.7° was obtained (Kajimoto, Yokoyama, Ooshima & Endo, 1991). The angles χ (121.5°) and φ (120.6°) in DMABN are larger than the values determined in MMD: 118.4° for χ and 119.2° for φ.

Cyano substituent

The cyano group in DMABN deviates from linearity, with an angle of 177.5 (4)°. Further, it is not located in the plane of the phenyl ring, as seen from the out-of-plane distances of 0.017 (5) and 0.037 (6) Å for C(9) and N(2) at 253 K, respectively. With ABN at 293 K (Merlino & Sartori, 1982), as well as at 153 K, a similar unexpected deviation from coplanarity for the phenyl and cyano groups is observed, with out-of-plane distances (153 K) of 0.020 (3) Å for C(7) and 0.047 (3) Å for N(2). These values are somewhat larger than those found above with DMABN. In the case of MHD, the out-of-plane distances in the cyano group are still larger than those of both DMABN and ABN. At 153 K, the following values are obtained: 0.053 (2) Å for C(7) and 0.122 (3) Å for N(2). In all structures, the cyano group is bent towards the substituent of the amino group. The phenyl ring apparently tends to decouple the cyano group, as well as that of the dimethylamino group (Yu & Jiang, 1991), as discussed above. The cyano group in many ways acts as a spectator group. The average length of bond 7 between the phenyl ring and the nitrile C atom in the five aminobenzonitriles is 1.424 Å, whereas for the cyano triple bond 8 a length of 1.148 Å is found (see Table 7). Both cyano bond distances obtained here are somewhat larger than the values of 1.401 (14) and 1.137 (14) Å reported for bonds 7 and 8 in benzonitrile crystals (Fauvet, Massaux & Chevalier, 1978).

Crystal packing and hydrogen bonding

The DMABN molecules in the crystal are arranged in stacks, with an alternating *A*-Ph-*D*/*D*-Ph-*A* molecular orientation (see Fig. 8). This packing can be brought about by the relatively large ground state dipole moment of 6.6 D for DMABN (Schuddeboom *et al.*, 1992). The absence of stacks in the case of MMD, with a dipole moment of 5.1 D (Kühnle & Zachariasse, unpublished results), may be due to the out-of-plane configuration of the dimethylamino group, which hinders the mutual approach of the MMD molecules.

With the compounds containing amino H atoms, ABN, MHD and HHD, weak hydrogen bonding occurs between the molecules in the crystal. This has previously been shown for ABN on the basis of nuclear quadrupole resonance measurements (Colligiani & Ambrosetti, 1977). The hydrogen

bonding leads to the formation of extended molecular networks in the crystals, in contrast to DMABN and MMD, where hydrogen bonding is obviously absent.

From the crystal packing of MHD depicted in Fig. 9 it is seen that two different intermolecular interactions occur. A hydrogen bond is present between the amino H atom and the cyano group of a neighbouring MHD molecule. The observed NH···NC distance of 2.30 (2) Å [N···N distance: 3.081 (2) Å] is consistent with a weak hydrogen bond (Emsley, 1980).This is supported by the non-linear N—H···N arrangement [angle 145 (2)°]. Further, the distance CH···NC of 2.510 (2) Å between the phenyl H atom H(8) and the N atom of the cyano group (see Fig. 9) of two MHD molecules in the crystal is indicative of a relatively weak long-range interaction, with a C···N distance of 3.424 (3) Å. The N···N distance in the high-temperature phase of the MHD crystal decreases with temperature (Table 7), from 3.127 (4) Å at 293 K to 3.081 (2) Å at 173 K. This means that the strength of the hydrogen bonding increases when lowering the temperature (see next section).

The crystal packing of HHD is depicted in Fig. 10, showing the presence of a layered structure. The
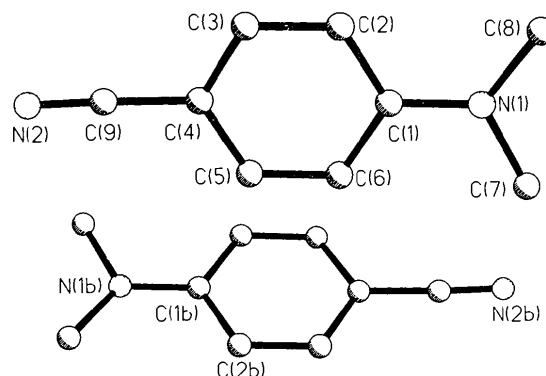

Fig. 8. Crystal packing of 4-(dimethylamino)benzonitrile (DMABN) at 253 K. The two molecules are part of a stack consisting of DMABN molecules with alternating orientations, see text.
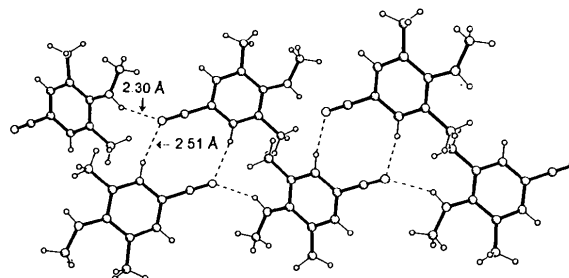

Fig. 9. Chain of 3,5-dimethyl-4-(methylamino)benzonitrile (MHD) molecules, formed by weak (Me)NH···NC hydrogen-bond linkages (2.30 Å). The long-range interaction (2.51 Å) between the phenyl H(8) atom and the cyano N(2) atom is also indicated, see text.

inter-layer distance is 4.59 (2) Å and each layer is displaced by an increment given by the monoclinic angle β (Table 1). The layers are in the form of a pattern consisting of squares and octagons. Each of the two amino H atoms in HHD interacts with an N atom of the cyano group of two different neighbouring HHD molecules. With ABN, in contrast, only one of the two amino H atoms forms such a hydrogen bond, with an N⋯N distance of 3.083 (3) Å, see Fig. 11 and Table 7. The hydrogen bond in HHD is longer [average N⋯N distance 3.180 (3) Å, average N—H⋯N angle 159 (2)°], and hence weaker than in ABN. This is possibly due to the more severe steric requirements set by the two methyl substituents on the benzene nucleus in *ortho* positions to the amino group.

Phase transitions

The crystal structures of all five compounds studied here undergo solid–solid phase transitions upon
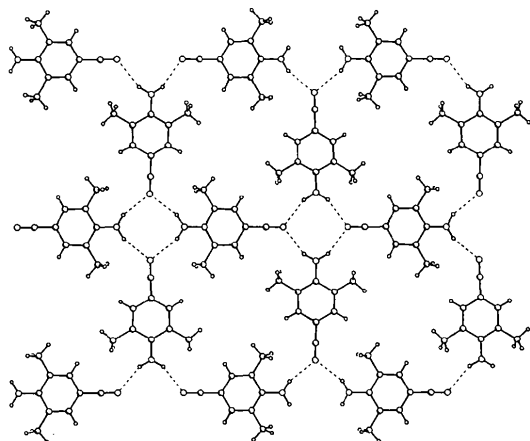

Fig. 10. A single layer of 4-amino-3,5-dimethylbenzonitrile (HHD) molecules. Each amino H atom is linked to a cyano N atom of two different neighbouring molecules, giving a tessellating pattern of octagons and squares.
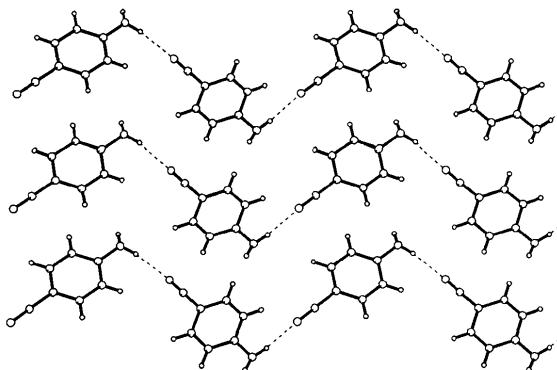

Fig. 11. Crystal packing of 4-aminobenzonitrile (ABN) at 153 K, showing the hydrogen bonding between an amino H atom and the cyano group of a neighbouring molecule.

cooling, as mentioned in *Experimental*. In order to elucidate the nature of these phase transitions, it was attempted to grow crystals at temperatures below these transitions. This only succeeded in the case of ABN, precluding measurements under low-temperature conditions for the four other molecules. Further attempts to grow crystals of these low-temperature phases are in progress.

From the crystallographic data at the various temperatures (Table 1), the following observations are made, showing that the structures change with temperature. In the low-temperature crystal phase of ABN, the lattice constants are different from those observed for the high-temperature phase. In the latter case, the space group is $P2_1/c$ (Merlino & Sartori, 1982), while for the low-temperature phase the space group $P2_12_12_1$ is found. Further, the monoclinic angle β in the crystal unit cell of DMABN and MHD decreases continuously upon lowering the temperature. A similar trend is observed with ABN, where the angle β equals 102.0 (1)° in the high-temperature phase (Merlino & Sartori, 1982), against the orthorhombic 90° angle in the low-temperature phase (Table 1). With MHD, the crystal structure approaches tetragonal symmetry when the temperature is lowered down to 173 K, as can be seen from the observation that the a and b axes become more and more equal.

Concluding remarks

The non-zero value of the inversion angle θ between the planes of the amino group and the phenyl ring in ABN [34 (3)°] and DMABN [11.9 (3)°] shows that the amino N(1) atom has pyramidal character. In the three 4-amino-3,5-dimethylbenzonitriles MMD, MHD and HHD, the magnitude of the twist angle around the N—phenyl bond [59.3 (2)°, 17.1 (6)° and 12 (4)°, respectively], as well as the out-of-plane displacement of the amino N atom with respect to the phenyl plane, see Table 7, is seen to be directly related to the steric requirements of the two methyl groups on the phenyl ring at positions *ortho* to the amino substituent. MMD is found to be different from the four other aminobenzonitriles, especially with respect to the configuration of the amino group, *the twist angle and the length of the N–phenyl bond*.

The crystal packing of DMABN, consisting of stacks of molecules in alternating orientations, is attributed to its relatively large dipole moment of 6.6 D, whereas in MMD (dipole moment 5.1 D) the formation of such stacks is thought to be prevented by the out-of-plane position of the dimethylamino group. Hydrogen bonding determines the overall crystal packing in ABN, MHD and HHD. With the last molecule, a layered structure consisting of squares and octagons is formed.

Note added in proof: In a recent paper (Gourdon, Launay, Bujoli-Doeuff, Heisel, Miehé, Amongal & Boillot, 1993), the structure of DMABN, determined at room temperature, is interpreted differently than in this paper.

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Structures of Racemic Monofluoro-Substituted Mandelic Acids, Their Relation to the Thermochemical Properties and an Analysis of Short Intermolecular Fluorine–Carbon Contacts

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Abstract

The structures of the three monofluoro-substituted mandelic acids ($C_8H_7FO_3$, $M_r = 170.14$) have been determined from low-temperature [122 (1) K] X-ray diffraction data [$\lambda(Cu\ K\alpha) = 1.54184$ Å].

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o-Fluoromandelic acid, monoclinic, $P2_1/c$, $a = 8.4238\ (12)$, $b = 5.4766\ (7)$, $c = 15.959\ (2)$ Å, $\beta = 95.962\ (11)°$, $V = 732.3\ (3)$ Å^3, $Z = 4$, $D_x = 1.543$ g cm^{-3}, $\mu = 11.25$ cm^{-1}, $F(000) = 352$, $R = 0.040$ for 1357 contributing reflections, m.p. 388.3 (5) K. m-Fluoromandelic acid (metastable modification), monoclinic, $P2_1/a$, $a = 10.8657\ (14)$, $b = 9.2663\ (10)$, $c = 15.722\ (2)$ Å, $\beta = 107.474\ (10)°$,