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The Crystal and Molecular Structure of N-Methylacetanilide

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The crystal structure of N-methylacetanilide has been determined from three-dimensional X-ray diffraction data. The crystals are orthorhombic, space group *Pnma*, and the molecule very likely has *m* symmetry. The N-methylacetamido-group is located in the space group mirror plane, and the benzene ring normal to it. The carbonyl group is *trans* to the benzene ring. The observed geometry of the molecule is discussed in some detail, and a comparison with the acetanilide molecule is made.

The conformation of N-methylacetanilide both in solution and in the solid state has been studied in connection with work on some related X-ray contrasting agents going on in our laboratory. A preliminary account of this work has been published earlier [1] but no details of the crystalline structure of N-methylacetanilide have been given. In this paper we will present the crystal structure of N-methylacetanilide as determined by X-ray diffraction methods and discuss in some detail the factors influencing the conformation.

The problem connected to the conformation of N-methylacetanilide is twofold: 1, As is well known, the amidogroup is planar [2] or nearly so [3] giving rise to two isomers (*cis* and *trans*). 2, The planes of the amidogroup and the benzene ring can make an arbitrary angle with each other.

In the X-ray contrasting agents studied [4] the acetamidogroup in the molecule is surrounded by two iodine atoms in the *ortho* positions. These large atoms force the acetamidogroup to be orthogonal to the benzene ring. Furthermore, these iodine atoms stabilize in some, still not clearly understood way, the *cis* and *trans* isomers, so that these can be chemically separated and isolated.

Due to the different orientation of the methylgroups in the two isomers relative to groups in the molecule which are magnetically anisotropic (the benzene ring and the carbonyl group), it is possible, unambiguously, to determine the actual conformation of each isomer from its NMR spectrum. In the investigation of these X-ray contrasting agents it was found that the unmethylated acetamidogroups preferentially were in the conformation with the carbonyl oxygen *cis* to the benzene ring, this conformation has been named endo- [5] (Fig. 1 a). When the acetamidogroup is methylated, however, the other conformation, named exo- [5] is found to be the most stable (Fig. 1 b).

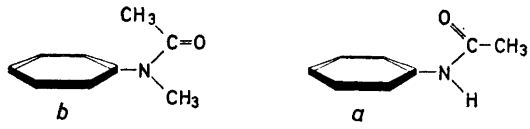

Fig. 1. Exo- and endo-conformation, schematic drawing.

The NMR spectrum of N-methylacetanilide, *i.e.* a compound without the *ortho* iodines, showed that also this compound preferentially (99.5 %) existed in the exo-conformation and with the plane of the acetamidogroup normal to the benzene ring.

To get more detailed information about the geometry of the N-methylacetamido group in the exo-conformation it was decided to solve the crystal structure. Brown and Corbridge [6,7] have earlier, in a thorough study, investigated the structure of acetanilide. In this compound the acetamidogroup is in the endo-conformation and nearly coplanar with the benzene ring. It was therefore thought that more detailed knowledge about the geometry of the N-methylacetanilide molecule might shed some light on the marked differences between the conformations of these two closely related molecules.

EXPERIMENTAL

Commercially available N-methylacetanilide was recrystallized from alcohol to give crystals suitable for X-ray diffraction work. The crystals grew as prisms elongated along the *b*-axis. The unit cell dimensions were determined from Guinier powder patterns using KCl as an internal standard. Various oscillation-, precession-, and Weissenberg-diagrams were used to establish the probable space group.

Crystal data: (λ—CuK_α = 1.5418 Å, λ—MoK_α = 0.7107 Å)
N-methylacetanilide, $C_6H_5N(CH_3)COCH_3$.
M.W. 149.2, m.p. 104°

Orthorhombic,

a = 17.151 Å, b = 7.328 Å, c = 6.779 Å (V = 851.98 Å^3)
D_M = 1.13 g/cm^3, Z = 4, D_x = 1.15 g/cm^3

Absorption coefficients for X-rays,

λ = 1.5418 Å, μ = 5.9 cm^{-1}
$F(000)$ = 320

Absent spectra:

hkl : none
$0kl$: $k + l = 2n + 1$
$hk0$: $h = 2n + 1$

Space group is $Pnma$ or $Pn2_1a$.

The intensities of the $h0l$ reflections were recorded on precession films using Zr-filtered Mo-radiation, and estimated visually: these data were used in a preliminary study of the *b*-axis projection. Later, partial three-dimensional intensity data were collected from multiple film equi-inclination Weissenberg diagrams taken rotating about the *b*-axis, and using Ni-filtered CuK_α radiation. The intensities of $h0l$, $h1l$, $h2l$, $h3l$, $h4l$, and $hk0$ layers were estimated visually, and brought on absolute scale. The intensities were corrected for Lorentz and polarization effects, and the structure amplitudes were derived. No absorption corrections were considered necessary. About 540 independent reflections were observed above background.

STRUCTURE ANALYSIS

The main difference between the two possible space groups is the mirror plane normal to the *b*-axis in *Pnma* which is reduced to a twofold screw axis in $Pn2_1a$. From the NMR conformational analysis of N-methylacetanilide in solution, the acetamidogroup and the benzene ring are found to be orthogonal.[1] If this conformation is conserved in the solid, a possible molecular arrangement could be compatible with the highest symmetrical of the two space groups. The arrangement would require the acetamidogroup to be located in the mirror plane and the benzene ring orthogonal to it.

The highest possible symmetry the molecule can achieve is a mirror plane. According to Kitaigorodskii [8] molecules of this type with very few exceptions (*β*-isoprene sulfone,[9] metanilic acid [10]) occupy general positions in the crystal, and their packing laws are like those of unsymmetrical molecules. This is noteworthy, since molecules of symmetry *mm* frequently retain one symmetry plane (in both cases, *i.e.* symmetries *m* and *mm*, the molecules surrender one symmetry plane to satisfy close packing requirements).

In the present case the actual space group is *Pnma*, giving, according to Kitaigorodskii,[8] a limiting close packing arrangement for molecules in special positions of symmetry *m*, hence, the true space group may be *Pnma*.

The projections along [010] might then give precise information on bond distances and angles in the acetamido group. Preliminary work was therefore started in the (*h*0*l*) projection.

As all the atoms are of about equal weight, inequalities [11] were used for phase determinations. However, it turned out that two acetamidogroups from adjacent molecules, spaced *b*/2 Å apart were overlapping heavily in this projection, and made determination of precise parameters impossible. The conformation, however, seemed to be correct.

A three-dimensional Patterson synthesis therefore was evaluated. The concentration of vector peaks in these maps supported the space group choice.[12] Information extracted from the Patterson maps, held together with the already existing information, led to a rough determination of atomic parameters which were subsequently successfully refined within the space group chosen, *Pnma*. The resulting reliability index $R = 0.082$. The refinement consisted of Fourier- and difference-syntheses, full matrix least squares refinement, first introducing isotropic- and later anisotropic- thermal parameters for the atoms.[13] When the reliability index had reached 0.13 a difference synthesis was calculated, where the contributions from all atoms except hydrogen were subtracted, and the aromatic hydrogen atoms were located.

Peaks were also observed where the methyl hydrogens were supposed to be situated, but these peaks were somewhat elongated in the *b*-axis direction, making it difficult to judge which of the peaks that were situated in the mirror plane. However, one of the two peaks in the vicinity of each methyl-carbon was more than twice as high in electron density as the other, and one is therefore led to believe that this peak is a superposition of two hydrogen atoms, one above and one below the mirror plane, but that the resolution in the difference map is too low to permit the two peaks to be well separated. A three-dimensional least squares refinement of all atoms, including hydrogen

with isotropic B-values, also gives hydrogen atom positions in accordance with this picture.

The temperature factors for the methyl-carbons are markedly more anisotropic and higher in the b-direction than the temperature factors for the other atoms, and some motion is evident.

Another plausible explanation of the high anisotropy of the methyl-carbons might be that the molecule deviates from the m symmetry, *i.e.* that the true space group is $Pn2_1a$ and not $Pnma$.

Refinement with isotropic temperature factors for the methyl-carbons was therefore tried within this space group. The two atoms were moved somewhat out of the mirror plane in $Pnma$. However, the result of the refinement was to bring the methyl-carbons back to the original location within standard devia-

Table 1. Positional parameters uncorrected for rigid body motion, and their standard deviations $\times 10^4$ in parentheses as fractions of the cell edges.

	x	σx	y	σy	z	σz
O	−0.0491	(3)	0.2500	(0)	−0.0759	(9)
N	0.0283	(4)	0.2500	(0)	0.1854	(11)
C	0.0191	(6)	0.2500	(0)	−0.0087	(15)
Me	−0.0379	(5)	0.2500	(0)	0.3143	(15)
Me	0.0898	(6)	0.2500	(0)	−0.1306	(15)
2 × C	0.2107	(3)	0.0830	(13)	0.4209	(8)
2 × C	0.1406	(3)	0.0830	(10)	0.3202	(7)
C	0.2440	(6)	0.2500	(0)	0.4680	(13)
C	0.1070	(4)	0.2500	(0)	0.2727	(11)
H	0.2922	(60)	0.2500	(0)	0.5225	(140)
H	0.0818	(70)	0.2500	(0)	−0.2545	(240)
H	−0.0308	(70)	0.2500	(0)	0.4523	(200)
H	0.2321	(42)	0.5569	(120)	0.4564	(127)
H	0.1102	(31)	0.5569	(105)	0.2842	(88)
2 × H	−0.0810	(32)	0.1729	(74)	0.3029	(85)
2 × H	0.1380	(41)	0.1729	(98)	−0.1132	(116)

Table 2. Vibration tensors.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
O	0.0819	0.1084	0.0958	0.0000	0.0000	−0.0456
N	0.1002	0.0856	0.0788	0.0000	0.0000	−0.0067
C	0.1210	0.0518	0.0840	0.0000	0.0000	−0.0062
Me	0.0393	0.2728	0.0918	0.0000	0.0000	0.0154
Me	0.0787	0.2388	0.0474	0.0000	0.0000	0.0030
C	0.0684	0.0818	0.0694	0.0000	0.0000	0.0030
C	0.0567	0.0719	0.0551	0.0000	0.0000	−0.0036
C	0.0781	0.0429	0.0737	0.0100	−0.0082	−0.0130
C	0.0781	0.0429	0.0737	0.0100	−0.0082	−0.0130
C	0.0910	0.0478	0.0790	0.0190	0.0000	−0.0065
C	0.0910	0.0478	0.0790	0.0190	0.0000	−0.0065

Table 3. Principal components of rigid body vibrations, with direction cosines referred to molecular axes.

	L	*M*	*N*
$T_1^2 = 0.0684$ Å^2	0.9507	0.3018	0.0706
$T_2^2 = 0.0534$ Å^2	0.1464	−0.2362	−0.9606
$T_3^2 = 0.0284$ Å^2	0.2732	−0.9236	0.2687
$\omega_1^2 = 12.5°$	0.9993	0.0002	0.0350
$\omega_2^2 = 3.9°$	−0.0345	0.1814	0.9827
$\omega_3^2 = 2.6°$	0.0059	0.9834	−0.1813

Table 4. Interatomic distances and angles ± standard deviations, before and after correction for rigid body motion.

	uncorrected	corrected	st. deviation
Distances in the acetamido group (Å)			
C−O	1.255	1.263	0.009
C−CH_3	1.468	1.503	0.010
C−N	1.325	1.344	0.009
N−CH_3	1.433	1.467	0.009
N−C_{arom}	1.474	1.481	0.009
C−H	0.94		0.11
2 × C−H	0.93		0.11
C−H	0.89		0.11
2 × C−H	1.01		0.11
C−C distances in the benzene ring (Å)			
C_1-C_2	1.388	1.415	0.010
C_2-C_3	1.387	1.392	0.008
C_3-C_4	1.388	1.407	0.010
C−H distances in the benzene ring (Å)			
2 × C_2−H	1.11		0.11
2 × C_3−H	1.17		0.11
C_4−H	0.91		0.11
Angles in the acetamido group (°)			
∠CH_3−C−O	124.4	124.5	0.6
∠CH_3−C−N	117.5	118.5	0.6
∠O−C−N	118.1	117.0	0.6
∠C−N−C_{arom}	120.5	119.6	0.6
∠C−N−CH_3	120.7	121.7	0.6
∠C_{arom}−N−CH_3	118.8	118.7	0.6
Angles in the benzene ring (°)			
∠$C_2-C_1-C_2$	123.6	122.8	1.3
∠$C_1-C_2-C_3$	118.2	118.6	0.7
∠$C_2-C_3-C_4$	118.2	118.7	0.7
∠$C_3-C_4-C_3$	123.6	122.6	1.3

Table 5. Observed and calculated structure factors.

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
2	-0	-0	31.33	34.25	12	-0	6	1.28	1.64	1	1	7	2.51	-3.33	6	3	0	10.86	-10.42
4	-0	-0	20.45	20.60	1	-0	7	2.54	3.60	2	1	7	1.44	-.95	8	3	0	7.48	-6.72
6	-0	-0	16.36	-16.84	2	-0	7	2.92	-2.73	3	1	7	2.48	-3.14	10	3	0	2.48	-2.39
8	-0	-0	12.20	12.21	3	-0	7	2.51	-2.63	8	1	7	1.25	-1.22	12	3	0	15.25	15.30
10	-0	-0	9.70	-9.97	6	-0	7	1.94	2.54	9	1	7	1.67	1.34	14	3	0	10.52	9.67
12	-0	-0	16.47	-16.96	7	-0	7	1.88	-1.91	10	1	7	1.89	2.13	16	3	0	3.18	-4.29
14	0	0	3.34	-4.04	8	-0	7	1.27	-.45	11	1	7	1.39	-.77	18	3	0	4.12	3.62
16	0	0	6.89	-6.70	9	-0	7	2.96	2.83	-0	2	-0	84.10	-87.55	0	3	1	10.54	-10.96
18	0	0	4.08	-3.51	11	-0	7	2.49	1.77	2	2	-0	71.30	-74.48	1	3	1	17.69	17.70
20	0	0	1.66	2.03	2	1	0	31.07	-33.19	4	2	-0	32.99	-34.70	2	3	1	22.80	19.52
1	-0	1	31.75	33.42	4	1	-0	20.27	20.78	6	2	-0	18.42	18.85	3	3	1	3.48	2.86
2	-0	1	50.75	-50.03	6	1	-0	28.74	22.38	8	2	-0	1.80	-.29	4	3	1	12.43	12.45
3	-0	1	62.15	62.40	8	1	-0	19.63	17.70	10	2	-0	7.67	7.53	5	3	1	10.53	-9.99
4	-0	1	23.32	22.45	10	1	-0	13.23	-14.17	12	2	-0	1.94	-.98	6	3	1	6.28	-6.21
5	-0	1	18.55	-16.76	12	1	-0	5.92	-6.65	14	2	-0	14.85	14.87	7	3	1	8.15	8.45
6	-0	1	8.41	7.03	14	1	-0	0.66	-10.43	16	2	-0	2.69	3.03	8	3	1	2.22	2.19
7	-0	1	6.76	7.66	16	1	-0	5.52	-5.31	1	2	1	48.35	-47.47	9	3	1	2.06	-1.72
8	-0	1	6.86	-6.85	-0	1	1	58.53	-57.64	2	2	1	11.90	-12.18	10	3	1	5.66	5.72
9	-0	1	16.67	-17.28	1	1	1	31.61	33.70	3	2	1	10.40	-7.65	11	3	1	12.17	12.26
10	-0	1	18.01	-19.24	2	1	1	7.75	-8.31	4	2	1	12.29	13.02	12	3	1	1.97	1.90
11	-0	1	7.09	7.68	3	1	1	38.26	-33.05	5	2	1	12.02	-11.92	13	3	1	2.86	-3.04
12	-0	1	2.75	2.77	4	1	1	5.23	-5.46	6	2	1	7.08	7.16	14	3	1	10.94	-10.39
13	-0	1	2.51	-2.44	5	1	1	0.23	0.21	7	2	1	5.45	4.86	15	3	1	2.72	2.70
14	-0	1	2.13	2.69	6	1	1	10.23	-9.06	8	2	1	3.23	3.50	2	3	2	6.07	-6.11
15	-0	1	2.17	-1.53	7	1	1	8.54	-8.46	9	2	1	2.59	1.76	3	3	2	20.15	-20.20
16	-0	1	1.54	-1.80	8	1	1	12.34	-12.01	10	2	1	3.92	3.18	4	3	2	5.87	-4.22
17	-0	1	1.50	1.54	10	1	1	2.73	2.72	11	2	1	3.23	2.96	5	3	2	12.74	12.78
18	-0	1	2.01	-.34	11	1	1	7.59	-8.32	12	2	1	6.06	6.18	6	3	2	7.80	-8.63
-0	-0	2	.44	-2.75	12	1	1	7.03	8.09	13	2	1	2.51	2.34	7	3	2	7.04	6.50
1	-0	2	51.83	54.35	13	1	1	7.53	-8.89	14	2	1	3.02	-3.24	8	3	2	11.16	12.20
2	-0	2	28.58	-30.97	14	1	1	3.36	3.89	15	2	1	3.65	-4.03	9	3	2	6.67	6.41
3	0	2	20.22	-18.76	15	1	1	4.84	-4.87	17	2	1	2.87	2.14	11	3	2	6.19	-6.97
4	-0	2	51.26	50.25	16	1	1	3.42	2.97	-0	2	2	6.14	-6.96	12	3	2	5.36	-5.20
5	-0	2	31.60	-32.95	18	1	1	1.40	.85	1	2	2	15.55	15.23	13	3	2	2.62	2.77
6	-0	2	9.38	-8.87	1	1	2	41.40	42.83	2	2	2	3.93	4.79	14	3	2	2.92	3.01
7	-0	2	36.44	-36.37	2	1	2	23.14	20.78	3	2	2	9.86	8.64	15	3	2	5.75	5.44
8	-0	2	8.82	-8.47	3	1	2	16.24	-12.24	4	2	2	9.61	-8.77	16	3	2	2.74	1.95
9	-0	2	11.31	-11.01	4	1	2	12.24	11.97	5	2	2	12.09	11.41	17	3	2	2.55	-2.34
12	-0	2	3.79	3.79	5	1	2	7.00	-7.75	6	2	2	1.45	-.75	18	3	2	2.29	1.16
13	-0	2	3.33	-3.85	6	1	2	18.87	-13.63	7	2	2	22.25	23.54	0	3	3	27.65	-26.27
14	-0	2	3.75	3.76	7	1	2	11.77	-12.22	8	2	2	8.67	-8.81	1	3	3	17.05	-15.87
15	-0	2	6.72	6.81	8	1	2	1.62	1.34	9	2	2	10.94	12.06	2	3	3	8.81	-8.26
16	-0	2	8.57	8.29	10	1	2	1.83	-3.16	10	2	2	10.24	11.13	3	3	3	6.24	-6.66
17	-0	2	2.54	3.19	11	1	2	6.97	-7.59	11	2	2	5.85	6.46	4	3	3	3.17	-3.57
18	-0	2	1.37	1.16	13	1	2	2.11	-1.73	12	2	2	4.98	-4.91	6	3	3	4.37	4.67
1	-0	3	18.50	16.92	14	1	2	2.64	-2.67	13	2	2	7.96	-7.31	8	3	3	6.96	6.78
2	-0	3	3.31	3.48	16	1	2	1.51	-.28	14	2	2	3.69	-3.77	9	3	3	0.56	-0.20
3	-0	3	9.11	-9.58	17	1	2	2.04	-2.52	16	2	2	4.62	-4.12	10	3	3	5.98	-4.97
4	-0	3	7.50	7.94	19	1	2	1.70	.38	17	2	2	1.39	-1.30	11	3	3	4.57	5.17
5	-0	3	5.74	-5.71	-0	1	3	44.87	26.15	19	2	2	1.12	-1.46	12	3	3	8.89	8.05
6	-0	3	34.88	-33.60	1	1	3	0.12	8.84	1	2	3	2.48	2.49	13	3	3	3.26	2.81
7	-0	3	13.60	13.56	2	1	3	36.94	32.91	2	2	3	5.53	-5.76	14	3	3	3.38	2.21
8	-0	3	3.12	1.59	3	1	3	1.79	3.96	3	2	3	7.82	-8.26	1	3	4	8.76	-9.12
9	-0	3	3.27	-3.35	4	1	3	16.49	-12.33	4	2	3	8.85	8.03	2	3	4	6.80	6.08
11	-0	3	6.66	-7.97	5	1	3	26.36	24.48	5	2	3	4.39	-3.79	3	3	4	3.84	-3.78
12	-0	3	8.08	7.76	6	1	3	2.01	-2.40	6	2	3	5.80	5.88	5	3	4	2.67	2.61
14	-0	3	6.36	5.84	7	1	3	2.73	2.26	7	2	3	4.95	4.31	6	3	4	3.34	2.58
15	-0	3	3.73	3.11	8	1	3	2.86	-4.08	8	2	3	10.12	11.23	7	3	4	11.35	-9.97
16	-0	3	1.47	1.51	10	1	3	2.80	-3.25	9	2	3	1.91	1.85	9	3	4	5.97	6.58
1	-0	4	3.79	3.73	11	1	3	1.45	-2.59	10	2	3	2.44	-1.87	10	3	4	7.87	7.66
3	-0	4	23.12	-10.69	12	1	3	3.67	-3.36	11	2	3	2.52	-2.32	11	3	4	6.02	5.68
4	-0	4	3.77	4.08	13	1	3	2.16	3.02	12	2	3	7.31	-7.18	12	3	4	2.03	1.72
5	-0	4	10.09	10.26	14	1	3	5.31	-4.64	13	2	3	1.51	2.02	0	3	5	3.16	2.37
7	-0	4	7.54	6.51	15	1	3	3.01	-1.69	14	2	3	3.35	-2.45	1	3	5	2.45	+2.92
8	-0	4	4.71	4.32	16	1	3	2.51	-1.68	16	2	3	2.40	-2.41	2	3	5	2.01	-2.36
11	-0	4	8.38	7.04	1	1	4	3.81	4.55	17	2	3	1.82	-1.11	3	3	5	7.70	7.52
12	-0	4	3.78	3.36	2	1	4	1.22	1.59	19	2	3	2.16	-1.68	4	3	5	7.89	-7.14
13	-0	4	8.60	8.30	3	1	4	8.57	9.26	0	2	4	8.45	-8.71	6	3	5	3.57	-2.90
14	-0	4	2.12	-1.92	4	1	4	2.83	-2.25	2	2	4	4.28	4.16	7	3	5	9.01	8.36
15	-0	4	1.43	1.11	5	1	4	13.05	11.93	4	2	4	9.87	-9.15	8	3	5	6.53	7.07
16	-0	4	2.32	2.77	6	1	4	2.99	-2.65	7	2	4	2.41	-1.20	9	3	5	8.47	8.53
1	-0	5	7.56	-7.13	7	1	4	7.04	-8.20	8	2	4	8.95	-8.60	12	3	5	2.93	2.47
2	-0	5	6.77	-6.93	8	1	4	6.98	-6.57	9	2	4	12.68	-11.56	6	3	6	7.95	8.62
3	-0	5	5.34	5.36	10	1	4	5.81	-6.28	13	2	4	3.31	-3.07	11	3	6	1.62	.39
4	-0	5	2.89	-3.37	11	1	4	1.78	-2.34	17	2	4	1.91	-1.62	3	3	7	3.76	4.20
5	-0	5	13.20	12.93	12	1	4	3.76	-3.65	1	2	5	1.82	.93	4	3	7	3.89	4.76
6	-0	5	8.96	-8.93	13	1	4	1.52	.23	2	2	5	8.18	7.66	2	3	8	1.86	2.83
7	-0	5	2.62	-3.33	-0	1	5	4.22	-2.78	3	2	5	2.49	-2.65	5	3	8	1.48	-1.68
8	-0	5	8.79	9.23	1	1	5	2.62	2.18	4	2	5	5.80	5.08	-0	4	-0	28.41	30.38
9	-0	5	3.45	4.02	2	1	5	7.08	7.94	5	2	5	3.28	-2.97	2	4	0	27.04	29.42
10	-0	5	3.08	1.83	4	1	5	2.05	1.78	6	2	5	3.93	-3.95	4	4	0	15.68	15.55
11	-0	5	2.16	3.35	5	1	5	10.59	-10.81	7	2	5	7.49	-7.51	6	4	0	7.34	-7.51
12	-0	5	1.49	-.99	6	1	5	7.45	6.84	8	2	5	2.13	-2.46	8	4	0	1.11	2.16
15	-0	5	1.24	2.30	7	1	5	15.10	-12.79	15	2	5	1.13	-2.21	14	4	0	9.00	-10.00
-0	-0	6	2.17	2.40	8	1	5	2.64	-3.33	-0	2	6	1.51	-1.89	1	4	1	22.54	20.26
1	-0	6	3.07	3.31	9	1	5	5.53	-4.30	3	2	6	3.99	4.40	2	4	1	.95	-1.14
2	-0	6	4.07	5.07	10	1	5	4.84	-5.41	4	2	6	6.02	-6.44	3	4	1	7.32	6.98
3	-0	6	5.55	-5.51	11	1	5	5.45	-4.41	7	2	6	2.94	2.74	4	4	1	12.13	-11.63
5	-0	6	3.45	-3.77	12	1	5	3.40	-3.61	10	2	6	1.34	-1.73	5	4	1	8.29	8.47
6	-0	6	3.77	3.91	4	1	6	3.07	-3.48	5	2	7	2.94	3.01	6	4	1	2.79	-2.94
7	-0	6	2.64	-2.24	8	1	6	6.71	-4.84	8	2	8	1.25	-1.74	7	4	1	1.06	-2.06
8	-0	6	5.43	4.39	10	1	6	2.44	-.52	2	3	0	17.28	-18.16	10	4	1	2.22	-1.99
9	-0	6	1.47	3.76	-0	1	7	4.36	-4.62	4	3	0	28.25	26.18	11	4	1	3.53	-3.31
10	-0	6	3.19	-3.27															

Table 5. Continued.

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
12	0	1	5.67	-6.19	11	0	2	1.94	-2.28	8	0	3	4.05	-7.57	8	0	4	3.67	4.08
14	0	1	2.21	2.98	12	0	2	3.68	3.51	10	0	3	3.66	2.70	9	0	4	6.38	6.62
0	0	2	4.51	4.89	13	0	2	0.39	0.41	11	0	3	3.11	2.67	10	0	4	2.01	-.25
1	0	2	7.71	-7.17	14	0	2	2.36	2.07	12	0	3	3.66	3.76	2	0	5	3.92	-3.61
2	0	2	.63	-.97	15	0	2	.02	-1.32	14	0	3	2.60	1.61	3	0	5	.98	1.76
3	0	2	3.60	-3.01	16	0	2	2.72	2.31	0	0	4	6.20	7.36	4	0	5	2.41	-2.26
4	0	2	8.79	8.74	2	0	3	2.90	2.52	2	0	4	2.21	-1.50	5	0	5	2.41	1.89
5	0	2	0.86	-0.41	3	0	3	0.34	0.04	4	0	4	1.86	2.23	6	0	5	2.41	2.69
6	0	2	3.85	3.34	4	0	3	3.06	-2.48	6	0	4	1.89	-1.67	7	0	5	5.16	5.19
7	0	2	9.36	-10.05	6	0	3	1.75	-1.59	6	0	4	1.92	-1.64	1	0	6	0.17	0.60
9	0	2	6.87	-6.06	7	0	3	2.56	-2.33	7	0	4	2.38	1.77	7	0	6	2.46	-2.24
10	0	2	6.79	-8.06															

tion. The conclusion reached at this point is therefore that the molecule crystallizes in the space group *Pnma* with marked anisotropic motion of the methyl groups with the largest amplitude in the direction orthogonal to the mirror plane. However, we will return to this question in the discussion.

The final atomic coordinates and their standard deviations are given in Table 1, and the vibration tensors U_{ij}, in Table 2. This table shows that the thermal parameters for all the atoms in N-methylacetanilide are fairly large, and they are larger than corresponding values determined for acetanilide. This is not unexpected as there are no hydrogen bonds connecting the different molecules in the structure of N-methylacetanilide. An analysis of the anisotropic thermal parameters for the different atoms in N-methylacetanilide in the form of rigid body vibration of the N-methylacetanilide molecule, as given by Cruickshank,[14] has therefore been undertaken, and the result of the analysis is given in Table 3.

Table 4 contains interatomic distances and valence angles calculated from the parameters uncorrected and corrected for librational motion.

The observed and calculated structure factors are listed in Table 5.

DISCUSSION

The composite Fourier map of N-methylacetanilide is shown in Fig. 2, and the partial difference map with the hydrogen atom peaks in Fig. 3.

The conformation found for solid N-methylacetanilide is the same as inferred being the stable in solution from the NMR investigations [1] and from predictions based on measurements of electric dipole moments,[15] planar acetamido group in the exo-conformation, with the plane of the acetamido group orthogonal to the benzene ring plane.

The planarity of the acetamido group and the orthogonality of the two planes follows directly from the space group symmetry, whereas the distinction between the exo- and endo-conformation easily can be made on the basis of the relative electron densities in the peaks in Fig. 2, and from the interatomic distances calculated.

The interatomic distances and angles in N-methylacetanilide are given in Table 4.

The N—C-distance is short, 1.344 Å, and reveals an appreciable double bond character, as observed also in other amides [7,16–19] where distances from 1.29—1.37 Å have been observed. The C—O distance is 1.263 Å, and is some-

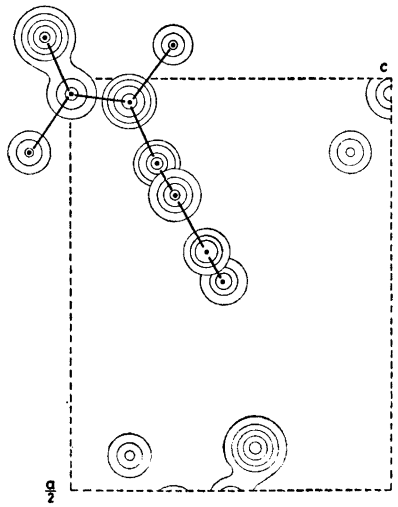

Fig. 2. N-Methylacetanilide; composite Fourier map.

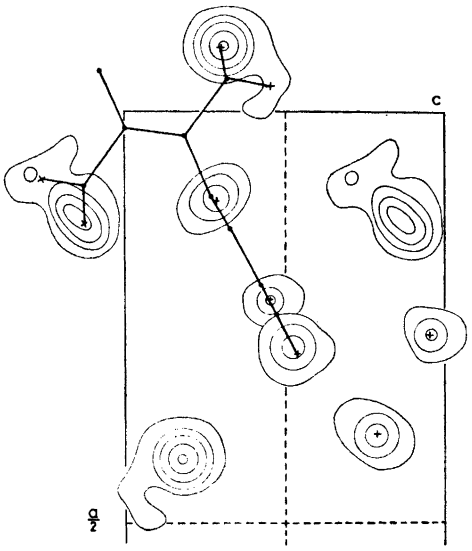

Fig. 3. N-Methylacetanilide; partial difference map with hydrogen atom peaks.

what longer than corresponding distances in related compounds where the average C—O distance is found to be 1.235 ± 0.005 Å.[20]

The N-methyl and C-methyl distances in N-methylacetanilide determined from the parameters uncorrected for rigid body motion are shorter than expected for single bonds between tetragonal-trigonal hybridized atoms, 1.433 Å and 1.468 Å compared to 1.472 Å and 1.506 Å.

When these bond lengths are corrected for rigid body vibration, however, the resulting values are 1.467 Å and 1.503 Å, and hence of normal values. The correction for thermal motion in the parameters of the methylcarbons seems very large, and is only justified by the reasonable distances derived on this basis.

Another plausible explanation to account for the observed anomalies of the methyl carbons, and at the same time preserve the mirror plane, might be a statistical distribution of the two methyl groups on each side of the mirror plane, but this explanation is merely another way of accounting for the observed extreme anisotropy of the motion.

The C_{arom}—N distance is determined to 1.481 Å and is of normal length for a C—N single bond distance. The distances and angles in the benzene ring are also of normal values.

The conformation of N-methylacetanilide is in Fig. 4 compared to the conformation found for acetanilide, also from a three-dimensional X-ray study.[6,7] In acetanilide the acetamidogroup is in the endo-conformation, and the two planar parts of the molecule make an angle of 17.6°. Hence, the conformation

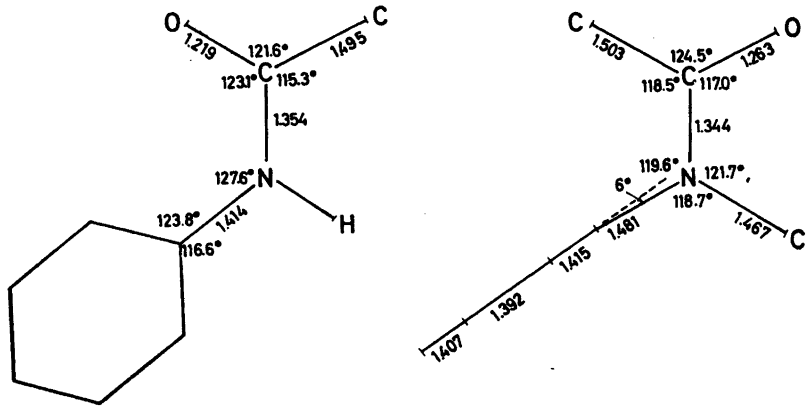

Fig. 4. Acetanilide and N-methylacetanilide; bond distances and angles.

of acetanilide is very different from the conformation observed for N-methylacetanilide.

The differences observed in bond lengths and angles in these two compounds are in accordance with expectations, considering the difference in molecular geometry. The low value of the dihedral angle in acetanilide makes π-electron communication between the benzene ring and the acetamidogroup possible. This effect is most clearly visualized in the shortening of the C_{arom}—N distance to 1.414 Å. The most pronounced change in angles is seen in the C_{arom}—N—C angle which is 127.6° in acetanilide and 119.6° in N-methylacetanilide. This difference may be explained as arising from steric hindrance effects which are different in the two compounds, and which are revealed in N-methylacetanilide by the bending of the C_{arom}—N-bond 6.4° off the benzene ring plane.

The change from the endo- to the exo-conformation when the acetamidogroup is methylated can be qualitatively explained as a result of steric effects.

In an amidogroup there seems to be a tendency for the two largest groups to occupy *trans* positions about the partial double C—N-bond. This is in accordance with the findings in acetanilide where the phenyl- and methylgroups are situated *trans* relative to one another, leading to the endo-conformation. This conformation has also been found to be realized in compounds where the methylgroup is interchanged with other larger groups.[21]

In N-methyl- and N-ethyl-formanilide the exo-conformation has been found to be preferred,[22] but also here the two largest groups, the phenyl- and the carbonyl-group, occupy *trans* positions about the partial double C—N-bond.

For N-disubstituted amidogroups, however, where also the C-atom has *two* substituents, the interaction between all four substituents has to be considered carefully. It is therefore difficult to give a simple explanation based on steric effects only, to account for the stable conformation found for N-methylacetanilide. Probably also charge distribution effects have to be included (interaction between polar groups).

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