

The Crystal Structure of the 1:1 Complex Benzenediazonium Chloride — Acetic Acid

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The crystal structure of the addition compound of benzenediazonium chloride with acetic acid, $C_6H_5N_2Cl \cdot CH_3COOH$, has been determined by three-dimensional X-ray diffraction analysis. The crystals are monoclinic, space group $P2_1/c$; the unit cell, containing four formula units, has the dimensions $a=8.080 \text{ \AA}$, $b=15.262 \text{ \AA}$, $c=8.381 \text{ \AA}$, and $\beta=103.50^\circ$.

Refinements of a trial structure were based on 804 independent reflections and carried out by least-squares methods, yielding a final R -value of 0.075.

The crystals are built up of benzenediazonium ions, chloride ions, and acetic acid molecules. The $C-C(N_2)-C$ angle in the benzene ring is found to be $124.0 \pm 0.5^\circ$, the $C-N$ bond length $1.425 \pm 0.006 \text{ \AA}$ and the $N-N$ triple bond $1.098 \pm 0.007 \text{ \AA}$. The N_2^+ group is coordinated to two chlorine ions in a linear arrangement with distances of 3.25 \AA from the centre of the N_2 group to the chlorine ions.

The acetic acid molecules are linked to chlorine ions by hydrogen bonds, the $O(H)-Cl$ distance being 3.01 \AA .

Hantzsch¹ has reported the existence of addition compounds between various diazonium salts and acetic acid. The compounds are formed from solutions of the diazonium salts in glacial acetic acid through precipitation with benzene. He claimed that ether cannot be used as a precipitating agent; the Knoevenagel procedure for forming benzenediazonium chloride yields the addition compound, however, when glacial acetic acid is used as the solvent and when the precipitation of the salt with use of ethyl ether is slow.² Hantzsch did not forward any theories about the way in which the acetic acid molecule is linked to the ions in the crystal, but his choice of diazonium salts to illustrate the complex forming ability indicates that he thought of the addition as one taking place between the diazonium ion and the acid.

In order to obtain information of the geometry of the benzenediazonium ion and also of the nature of the acetic acid complex a crystal structure determination of the benzenediazonium chloride-acetic acid addition compound was undertaken.

EXPERIMENTAL

Benzenediazonium chloride was prepared according to the Knoevenagel method with glacial acetic acid as the solvent. By letting ethyl ether mix slowly with the solution the addition compound precipitated as colourless, needle-shaped crystals. Hantzsch¹ stated the melting point to be 16.6°C for the compound. The crystals are unstable when exposed to X-rays and very hygroscopic.

The X-ray photographs were taken at temperatures about -10°C, the crystals being kept in thin-walled pyrex capillary tubes.

The dimensions of the unit cell were determined from measurements on oscillation, Weissenberg and precession photographs employing least-squares procedures.

The intensity data were obtained from photographs taken on an integrating Weissenberg camera with a crystal rotating about the needle axis (*c*). Equi-inclination diagrams of layers with *l* up to 3 were taken, using the multiple film technique (CuK α -radiation). In order to bring the intensities from the various layers on a common scale, intensity data of the (*h*0*l*) and (0*kl*) zones were collected by means of precession photographs (MoK α -radiation). 804 reflections were recorded, of which 149 were at background level.

The intensities were corrected with the Lp^{-1} factor. No absorption corrections were applied. Prior to the last stage of the refinement procedure the intensities were corrected for secondary extinction by the method given by Zachariassen² using a computer program written by A. Christensen for UNIVAC 1107. The full-matrix least-squares program used in the refinement procedure was written by Chr. Rømming for the computer CD 3300. The program minimizes the sum of the weighted squares of the differences between observed and calculated structure factors. The weight applied to the structure factors was constant for $|F_o| \leq 6$ and proportional to $|F_o|^{-3}$ for larger values. Non-observed reflections were included with a structure factor corresponding to the most probable value⁴ and assigned a weight of one third of the weight given to the observed reflections. The weight assignments turned out to give satisfactory results in the weight analysis. The program for three-dimensional Fourier calculations was written by Gantzel and Hope and the program for rigid-body analysis of the thermal vibrations by F. Gram.

The atomic form factors used in the calculations were those given by Hanson *et al.*⁵ for chlorine, oxygen, nitrogen, and carbon, and by Steward *et al.*⁶ for hydrogen.

CRYSTAL DATA

Benzenediazonium chloride-acetic acid, C₆H₅N₂Cl·CH₃COOH, m.p. 16.6°C.¹
Monoclinic, unit cell constants (-10°C)

$a=8.080$ (.007) Å; $b=15.262$ (.007) Å; $c=8.381$ (.008) Å; $\beta=103.50$ (.02)°

Figures in parenthesis are estimated standard deviations.

$V=1033.4$ Å³, $M=200.63$, $F(000)=416$, $Z=4$.

Calculated density: 1.29 g cm⁻³.

Absent reflections: $h0l$ when $l=2n+1$

$0k0$ when $k=2n+1$

Space group $P2_1/c$

STRUCTURE DETERMINATION

The positions of the chlorine atom and the benzene ring were determined from a sharpened [001] Patterson projection. Successive Fourier refinements revealed also the positions of the remaining non-hydrogen atoms and two-dimensional least-squares refinement calculations yielded a conventional *R*-factor of 0.11 for the (*hk*0) data. Overlapping of atoms occurred mainly in the acetic acid molecule.

Table 1. Continued.

Table with multiple columns of numerical data, organized in a grid-like structure. The data is presented in a series of rows and columns, with some values appearing in bold or with specific markers.

Approximate z parameters could be estimated from a three-dimensional Patterson synthesis. After a couple of least-squares cycles with refinement of positional and isotropic thermal parameters of the heavier atoms, a difference Fourier map was calculated. All hydrogen atoms except those belonging to the methyl group were localized and included in the further least-squares refinement. After some cycles, in which anisotropic thermal parameters were introduced for the heavier atoms, a second difference Fourier map was calculated. Only very diffuse maxima were found near the methyl carbon atom of the acetic acid molecule; this may be explained by a fairly free oscillation of the methyl group about the C—C bond. Parameters were assigned to the methyl hydrogen atoms assuming normal bond lengths and angles.

Least-squares refinement was then continued, adjusting the positional and anisotropic thermal parameters of Cl⁻, O, N, and C; hydrogen atoms were included in the structure factor calculations with $B=5.0 \text{ \AA}^2$, but their parameters were not refined. Prior to the last few cycles the observed structure factors were subjected to secondary extinction corrections. The final least-squares refinement calculations resulted in a conventional R -factor of 0.075 for the observed reflections.

The calculations were based on 804 reflections; the over-all scale factor, 39 positional and 78 thermal parameters were adjusted in the least-squares procedure, giving an overdetermination ratio of 6.8. The measured and calculated structure factors are listed in Table 1. The final positional and thermal parameters are presented in Tables 2 and 3.

Table 2. Final fractional positional parameters and their estimated standard deviations (in parenthesis).

Atom	x	y	z
Cl	0.1500 (.0002)	0.0933 (.0001)	0.3393 (.0004)
O(1)	0.1690 (.0008)	0.3774 (.0003)	0.4051 (.0011)
O(2)	0.2513 (.0007)	0.4952 (.0003)	0.5557 (.0013)
N(1)	0.0915 (.0008)	0.2721 (.0003)	0.1091 (.0012)
N(2)	0.2297 (.0008)	0.2647 (.0004)	0.1474 (.0014)
C(1)	0.9119 (.0008)	0.2810 (.0003)	0.0667 (.0013)
C(2)	0.8413 (.0009)	0.3627 (.0004)	0.0783 (.0015)
C(3)	0.6692 (.0009)	0.3694 (.0004)	0.0352 (.0014)
C(4)	0.5679 (.0009)	0.2979 (.0005)	-0.0299 (.0015)
C(5)	0.6453 (.0010)	0.2170 (.0004)	-0.0440 (.0017)
C(6)	0.8168 (.0009)	0.2070 (.0004)	0.0084 (.0015)
C(7)	0.2325 (.0009)	0.4501 (.0004)	0.4174 (.0017)
C(8)	0.2856 (.0010)	0.4981 (.0004)	0.2856 (.0019)
H(1)	0.940	0.408	0.131
H(2)	0.611	0.429	0.068
H(3)	0.441	0.304	-0.077
H(4)	0.578	0.162	-0.073
H(5)	0.884	0.153	-0.009
H(6)	0.274	0.468	0.674
H(7)	0.340	0.445	0.220
H(8)	0.369	0.566	0.328
H(9)	0.182	0.551	0.207

Table 3. Final thermal parameters and their estimated standard deviations (in parenthesis). The temperature factor is of the form $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl) \times 10^{-5}$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	1982 (39)	306 (6)	1743 (154)	-62 (18)	524 (101)	-24 (30)
O(1)	3172 (141)	442 (22)	1492 (303)	-693 (81)	645 (290)	50 (115)
O(2)	2692 (133)	357 (22)	1731 (446)	-323 (72)	32 (312)	306 (115)
N(1)	1889 (118)	306 (19)	1398 (346)	26 (68)	287 (300)	279 (104)
N(2)	1797 (124)	465 (27)	3198 (475)	26 (81)	336 (362)	80 (130)
C(1)	1581 (119)	339 (23)	1122 (391)	25 (74)	134 (324)	3 (121)
C(2)	2052 (144)	316 (24)	2671 (421)	181 (82)	626 (368)	68 (135)
C(3)	1859 (143)	440 (29)	1894 (415)	332 (89)	521 (386)	288 (141)
C(4)	1524 (136)	670 (39)	2098 (464)	165 (103)	578 (396)	46 (183)
C(5)	2184 (160)	510 (33)	2521 (485)	-322 (104)	1342 (414)	-116 (173)
C(6)	1925 (140)	375 (26)	2685 (453)	-137 (86)	1466 (397)	-96 (143)
C(7)	1987 (146)	326 (28)	2302 (468)	-209 (89)	205 (380)	244 (174)
C(8)	2464 (171)	492 (33)	2270 (578)	-70 (102)	751 (432)	681 (157)

An examination of the directions and amplitudes of the anisotropic atomic vibrations indicated that the benzenediazonium ion could reasonably be treated as a vibrating rigid body. The methods of Cruickshank^{7,8} were applied to find the translation and libration of the ion and to correct the intraionic distances for thermal foreshortening. Table 4 summarizes the results obtained by the thermal analysis.

Table 4. Results of the rigid body thermal analysis.

Translational tensor T (\AA^2)	0.5849	0.00156	0.00584
		0.04426	-0.00830
			0.04122
Principal axes of T and their direction cosines relative to the inertial axes.			
Axis	R.M.S. amplitude	$\cos a_1$	$\cos a_2$
1	0.246 \AA	.9445	.2492
2	0.225 \AA	-.0733	.7951
3	0.182 \AA	.3203	-.5529
Librational tensor ω (rad.^2)	0.0237	-0.00207	0.00391
		0.00698	0.00012
			0.00300
Principal axes of ω and their direction cosines relative to the inertial axes.			
Axis	R.M.S. amplitude	$\cos \theta_1$	$\cos \theta_2$
1	8.9°	.9778	.0923
2	4.7°	-.1137	.9879
3	2.7°	.1763	.1248
			-.9764

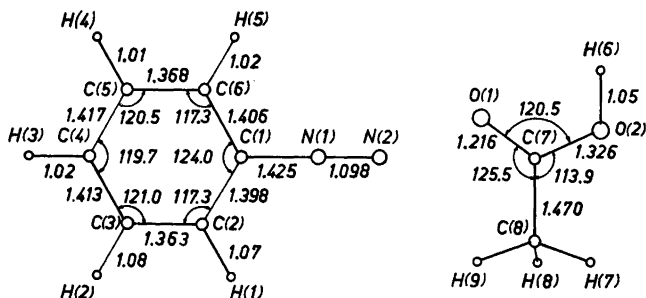


Fig. 1. Bond lengths and valence angles in the benzenediazonium ion and the acetic acid molecule.

DISCUSSION

The intramolecular distances and valence angles in the benzenediazonium ion (corrected), and the acetic acid molecule are shown in Fig. 1. They are also listed with their standard deviations in Table 5. Intermolecular and interionic distances are given in Table 6.

Table 5. Intramolecular distances (Å) and valence angles (°) and their estimated standard deviations.

Atoms	Distance (uncorrected)	Distance (corrected)
N(1)—N(2)	1.093 (0.007)	1.098
N(1)—C(1)	1.418 (0.006)	1.425
C(1)—C(2)	1.384 (0.007)	1.398
C(2)—C(3)	1.356 (0.007)	1.363
C(3)—C(4)	1.396 (0.010)	1.413
C(4)—C(5)	1.402 (0.010)	1.417
C(5)—C(6)	1.360 (0.008)	1.368
C(6)—C(1)	1.389 (0.009)	1.406
C(1)—C(4)	2.719 (0.007)	2.733
C(2)—C(5)	2.784 (0.010)	2.818
C(3)—C(6)	2.782 (0.008)	2.811
C(7)—C(8)	1.470 (0.016)	
C(7)—O(1)	1.216 (0.008)	
C(7)—O(2)	1.326 (0.016)	
	Angle	Angle (corrected)
C(6)—C(1)—C(2)	123.6 (0.5)	124.0
C(1)—C(2)—C(3)	118.0 (0.6)	117.3
C(2)—C(3)—C(4)	121.1 (0.6)	121.0
C(3)—C(4)—C(5)	119.3 (0.5)	119.7
C(4)—C(5)—C(6)	120.7 (0.7)	120.5
C(5)—C(6)—C(1)	117.5 (0.5)	117.3
C(1)—N(1)—N(2)	177.5 (1.1)	
C(8)—C(7)—O(1)	125.5 (1.2)	
C(8)—C(7)—O(2)	113.9 (0.7)	
O(1)—C(7)—O(2)	120.5 (1.0)	

Table 6. Intermolecular and interionic distances (Å).

N(1)—Cl	3.312	N(2)—O(1)	2.890
N(2)—Cl	3.215	N(1)—O(1)'	3.003
N(1)—Cl'	3.171	N(2)—O(1)'	2.933
N(2)—Cl'	3.317	O(2)—Cl	3.009
N(1)—O(1)	2.899	H(6)—Cl	2.11

The structure is composed of benzenediazonium ions, chlorine ions, and acetic acid molecules.

The benzenediazonium ion has, within the accuracy of the measurement, $2mm$ symmetry. All carbon and nitrogen atoms are situated less than 0.03 Å from a least-squares plane through these atoms. The C(4), C(1), N(1), and N(2) atoms are nearly on a straight line; and the pairs of bonds in the benzene ring mutually opposite this line are equal within the standard deviation. The bonds C(1)—C(2), C(1)—C(6), C(3)—C(4), and C(4)—C(5) are not different from the benzene carbon-carbon bond length, whereas C(2)—C(3) and C(5)—C(6) are possibly shorter than the benzene value.

The angles in the phenyl ring are distorted relative to hexagonal symmetry, in close analogy with findings in other benzenediazonium salts.^{2,9} The angle at C(1) is larger by 4° than in benzene itself, whereas at C(2) and C(6) the angle is by 2.7° less than 120°. The C(1)—C(4) diagonal (2.733 Å) is significantly shorter than the two other diagonals (2.818 Å and 2.811 Å).

The C(1)—N(1) bond is found to be longer (1.425 Å) than in benzenediazonium chloride (1.385 Å)² but equal in length to that observed in the 1,4-benzenebisdiazonium ion (1.42 Å).⁹ The N—N triple bond length (1.098 Å) corresponds to that found in these compounds.

The C—H bond lengths in the phenyl group are all in the range 1.01—1.08 Å with a mean value of 1.04 Å.

The N_2^+ group is coordinated to two chlorine ions in an approximately linear arrangement. One of the chlorine ions is closer to N(1) (3.171 Å) than to N(2) (3.317 Å), whereas the other is closer to N(2) (3.215 Å) than to N(1) (3.312 Å). The line connecting the chlorine ions passes through a point in the N—N bond nearly midway between the nitrogen atoms and forms an angle of about 40° with the plane of the benzene ring. There is thus no carbon-chlorine hydrogen bond from the *ortho* positions as was the case in benzenediazonium chloride.²

The N_2^+ group has two additional intermolecular contacts with carbonyl oxygen atoms of neighbouring acetic acid molecules. The four N—O distances are in the range 2.89—3.00 Å, values to be expected for van der Waals' contacts.

The carbon and oxygen atoms of the acetic acid molecule are coplanar. Bond lengths and angles are in good agreement with the values found for acetic acid itself,¹⁰ except for the C—C bond which comes out shorter in the present investigation (1.47 Å as compared to 1.54 Å). An intermediate value of 1.50 Å would be expected for an sp^3 - sp^2 single carbon-carbon bond.

The acetic acid molecule is hydrogen bonded to the chlorine ion, the O(2)—Cl⁻ separation being 3.009 Å. The O(2)—H(6) bond length is found equal to 1.05 Å and the H(6)—Cl⁻ distance 2.11 Å. The O—H—Cl⁻ angle is 142°.

The coordination polyhedron around the chlorine ion is a distorted pentagonal bipyramid. The bonds pointing towards the apices are the hydrogen bond from an acetic acid molecule and one ionic interaction with a diazonium group. In the equatorial plane there are the other ionic bond, two van der Waals' contacts with methyl groups and two contacts with hydrogen atoms of neighboring benzenediazonium ions.

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