

The Geometry of an *N*-Aryl-alkylnitrilium Ion. Low Temperature X-Ray Study of *N*-(2,6-Dimethylphenyl)-acetonitrilium Tetrafluoroborate

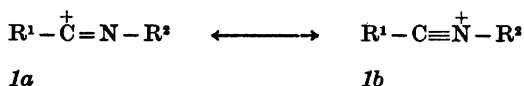
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The crystal structure of the title compound has been determined by X-ray methods using 1628 observed reflections collected by counter methods from a crystal kept at $-169\text{ }^{\circ}\text{C}$. The crystals are orthorhombic, space group *Pnma*, with unit cell dimensions $a = 19.858(14)\text{ \AA}$; $b = 6.780(2)\text{ \AA}$; $c = 8.042(2)\text{ \AA}$. The structure was solved by direct methods and refined to a conventional *R*-factor of 0.073; standard deviations in bond lengths are 0.003–0.004 \AA and in angles 0.2° where non-hydrogen atoms are involved. The tetrafluoroborate ion is disordered both at room temperature and at liquid nitrogen temperature. The nitrilium group has a nearly linear C–N–C–C arrangement with the central C–N bond length corresponding to a triple bond. The charge distribution is discussed on the basis of results from CNDO calculations.

The term “nitrilium salt” was adopted by Hantzsch in 1931 for compounds which he assumed would be formed by the reaction of nitriles with acids.¹ *N*-Substituted nitrilium salts were actually isolated 25 years later;^{2,3} the existence of protonated nitrilium salts of the type $[\text{R}-\text{C}\equiv\text{NH}]^+\text{X}^-$ (where X^- is an anion of the type SbCl_6^-) has also been reported.⁴

Nitrilium ions have been assumed to be intermediates in certain reactions, *e.g.* in the Ritter reaction⁵ and others involving nitriles and organic halides. Their electronic structure is usually described by formulae *1a* or *1b*



The ion reacts normally as a carbonium ion (*1a*) with nucleophilic reagents. From NMR data (including ^{13}C and ^{15}N resonance data) Olah and Kiovsky concluded that both protonated nitriles and *N*-alkylnitrilium ions appear to have linear configuration (*1b*) in solution (SO_2), however, and that the imino-carbonium form (*1a*) is only a minor contributor to the structure.⁶

To investigate the geometry of the nitrilium group in the solid state an *N*-phenylacetonitrilium ion was chosen for X-ray structure determination. In order to avoid ring closure through condensation to a quinazolinium salt the *ortho* positions of the phenyl ring were substituted by methyl groups.⁷ Although the tetrafluoroborate is extremely hygroscopic, this salt was used in order to avoid the heavier atoms of the more stable salts (*e.g.* SbCl_6^-) which would impair the accuracy of determination of the structural parameters of the cation.

EXPERIMENTAL

Crystals of the title compound were prepared from 2,6-dimethylphenyldiazonium tetrafluoroborate and acetonitrile.⁸ It was found necessary to work with substances of high purity and to control the temperature carefully in the last stages of the synthesis. The optimal temperature for the reaction of the diazonium salt with acetonitrile was found to be $35 \pm 2\text{ }^{\circ}\text{C}$ in order to avoid excessive formation of by-products. To form crystals of good quality the reaction was stopped as soon as the product started to precipitate. Colourless crystals were

isolated as long hexagonal needles or hexagonal plates by slow diffusion of ethyl ether into the filtered solution at 4 °C. The crystals are very reactive; in contact with air a layer of white powder is immediately formed on the surface, and decomposition of the crystals is complete after a couple of seconds.

X-Ray data were collected at 18 ± 1 and -169 ± 2 °C. At the higher temperature the crystal (approximately of cubic shape, edge 0.4 mm) was kept in a sealed capillary; at the low temperature the crystal was fairly stable in the cold nitrogen stream without protection.

Oscillation and Weissenberg photographs showed the crystal to be orthorhombic; systematically absent reflections indicated the space group $Pna2_1$ or $Pnma$. For the measurement of cell dimensions and collection of intensity data a SYNTEX PI diffractometer was used with graphite crystal monochromated $MoK\alpha$ radiation ($\lambda = 0.71069$ Å).

The room temperature data were collected using the $\theta/2\theta$ scanning mode with scan speeds (2θ) of $3-8^\circ \text{ min}^{-1}$ depending on the peak intensity. Reflections with $2\theta > 40^\circ$ were measured only if a quick scan gave an intensity larger than a preset value. The scan range was $\pm 1.0^\circ$ appropriately expanded to cover the effects of α_1, α_2 splitting; background counts were taken for 0.35 times the scan time at each end of the scan. Three standard reflections were measured after every 50 reflections; the data set was adjusted to compensate for a slow decrease in the intensity of the standard reflections during the data collection. The estimate of the standard deviations of the measurements was based on counting statistics with an additional term of 2% of the net intensity.

Reflections having an intensity larger than $2.5\sigma(I)$ were regarded as observed and used for the structure determination. No correction for absorption or secondary extinction was carried out.

Owing to severe thermal effects only 508 unique reflections were observed; this is less than one third of the theoretical number for $\sin \theta/\lambda > 0.7 \text{ \AA}^{-1}$. In order to obtain a better data set the experiment was repeated with a crystal held at -169 ± 2 °C. The procedure was the same as for the room temperature data collection except for the scan range ($\pm 1.2^\circ$) and the scan speed ($2-8^\circ$). The resulting low temperature data set comprises 1628 observed reflections with $\sin \theta/\lambda < 0.85 \text{ \AA}^{-1}$.

A description of the computer programs used is given in Ref. 8. The quantity minimized in the full-matrix least-squares program was $\sum w\Delta F^2$ where w is the inverse of the variance of the observed structure factor. Atomic form factors of Doyle and Turner⁹ for F, N, B, and C and of Stewart, Davidson and Simpson¹⁰ for H were used.

CRYSTAL DATA

N-(2,6-Dimethylphenyl)-acetonitrilium tetrafluoroborate, $C_{10}H_{12}NBF_4$, orthorhombic.

18 ± 1 °C : $a = 20.242(2)$ Å; $b = 7.035(1)$ Å; $c = 8.116(1)$ Å;

$V = 1155.7$ Å³; $D_{\text{obs}} = 1.3$ g cm⁻³; $D_{\text{calc}} = 1.339$ g cm⁻³

-169 ± 2 °C: $a = 19.858(14)$ Å; $b = 6.780(2)$ Å; $c = 8.042(2)$ Å;

$V = 1082.8$ Å³; $D_{\text{calc}} = 1.429$ g cm⁻³

$M = 233.03$; $F(000) = 480$; $Z = 4$. Absent reflections: $(0kl)$ for $k+l$ odd and $(hk0)$ for h odd.

Space group $Pnma$ (No. 62).

STRUCTURE DETERMINATION

The crystal structure was determined from the room temperature data. Intensity statistics gave strong evidence for a centric structure and thus for space group $Pnma$. The structure was solved by a combination of Patterson and direct methods and refined by Fourier and least-squares techniques.

The initial model was one of a nitrilium ion with all the atoms of the carbon-nitrogen skeleton situated on a crystallographic mirror plane and a tetrahedral tetrafluoroborate ion with the boron and two fluorine atoms in the mirror plane. As the refinement procedure progressed, it emerged that although the parameters of the cation were satisfactory, abnormally high thermal parameters for the BF_4^- ion suggested a disordered anion. A new model for this ion was therefore tried, *viz.* splitting the

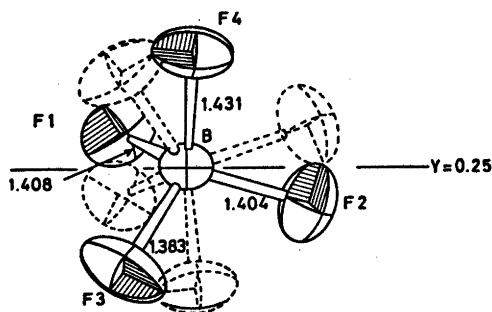


Fig. 1. The two "half" tetrafluoroborate ions. Distances (Å) are corrected for thermal libration.

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations obtained from the low temperature data. The temperature factor is $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$ for the nonhydrogen atoms.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
F1	.2898(1)	.2987(4)	.2482(3)	.0333(8)	.242(11)	.096(3)	.044(4)	-.043(2)	-.060(8)
F2	.3882(1)	.1917(4)	.3527(3)	.0194(6)	.330(12)	.169(4)	.046(3)	.025(3)	.061(9)
F3	.2920(2)	.1067(5)	.4785(5)	.0362(9)	.195(8)	.129(5)	-.078(6)	.038(5)	-.037(9)
F4	.3278(2)	.4197(5)	.4933(4)	.0351(9)	.116(5)	.087(3)	-.014(5)	-.010(4)	-.011(7)
B	.3249(1)	.25	.3923(3)	.0161(7)	.115(5)	.074(3)		-.004(3)	
N	.1424(1)	.25	.7159(2)	.0167(6)	.098(4)	.068(3)		-.053(2)	
C1	.0762(1)	.25	.6553(3)	.0143(6)	.088(4)	.066(3)		-.039(2)	
C2	.0245(1)	.25	.7725(3)	.0161(6)	.100(4)	.062(3)		-.006(2)	
C3	-.0403(1)	.25	.7110(3)	.0153(7)	.115(5)	.077(3)		.086(2)	
C4	-.0518(1)	.25	.5402(3)	.0147(7)	.106(4)	.084(3)		-.024(2)	
C5	.0003(1)	.25	.4286(3)	.0160(6)	.110(4)	.065(3)		-.085(2)	
C6	.0669(1)	.25	.4830(3)	.0154(6)	.090(4)	.063(3)		-.043(2)	
C7	.1948(1)	.25	.7708(3)	.0175(7)	.100(4)	.065(3)		.049(2)	
C8	.2617(1)	.25	.8381(3)	.0166(7)	.145(5)	.086(4)		-.127(3)	
C9	.0390(2)	.25	.9556(3)	.0224(9)	.171(6)	.059(3)		-.044(3)	
C10	.1239(2)	.25	.3623(3)	.0174(7)	.159(6)	.084(3)		.112(3)	

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H3	-.078(2)	.25	.781(4)	2.7(4)	H91	-.007(2)	.25	1.013(5)	4.4
H4	-.096(2)	.25	.507(4)	2.7	H92	.066(1)	.132(4)	.983(3)	4.4
H5	-.013(2)	.25	.306(5)	2.7	H101	.160(3)	.25	.397(6)	4.4
H81	.259(2)	.25	.952(6)	4.4(3)	H102	.124(1)	.140(4)	.284(3)	4.4
H82	.285(1)	.134(4)	.812(3)	4.4					

fluorine atoms into two "half" atoms to account for the thermal motion following the argument of Kartha and Ahmed.¹¹ A drawing of this model, in which the tetrahedral arrangement is maintained for each of the two halves, and seen along the mirror plane, is shown in Fig. 1. Even after the introduction of anisotropic thermal parameters for all non-hydrogen atoms, refinement did not reduce the *R*-factor to below 0.13. The goodness of fit $S = [\sum w\Delta^2/m - n]^{1/2}$ was 8.5, indicating systematic errors in ΔF , probably originating in a poor structure model. The resulting bond lengths and angles were not acceptable.

The low-temperature data set collected at this stage was introduced. It turned out, however, that the refinement of an ordered model converged to a conventional *R*-factor as high as 0.15, but introduction of the disordered BF_4^- -model lowered the *R*-value to 0.10. Obviously the cooling of the crystals had not resulted in an ordering of the structure. The hydrogen atoms were located and refined using isotropic thermal parameters; the least-squares

calculations terminated with a conventional *R*-factor of 0.073, $R_w = 0.086$ and $S = 3.6$.

The final atomic parameters are listed in Table 1. The observed and calculated structure factor data are available from the authors.

A difference Fourier map showed electron densities between -0.35 and $0.20 \text{ e } \text{\AA}^{-3}$. The structure refinement was repeated with necessary modifications in space group $Pna2_1$, but the results gave no justification for a change of space group. Interchange of atomic scattering factors for the C and N atoms of the nitrilium group resulted in abnormal thermal parameters for both atoms. We conclude therefore that the original assignment was correct.

Analysis of the thermal parameters in terms of rigid-body motion yielded r.m.s. ΔU values of $7 \times 10^{-4} \text{ \AA}^2$ and $18 \times 10^{-4} \text{ \AA}^2$ for the tetrafluoroborate ion and the nitrilium ion, respectively.¹² For the BF_4^- ion the largest r.m.s. amplitudes of libration are those about directions nearly parallel to the *a* and *b* axes, 10.5 and 8.1° , respectively, whereas that about the *c* axis is 3.8° . The fairly large amplitudes tend

Table 2. Bond lengths (Å) and angles (°).

Bonds		Angles	
B-F1	1.391	F1-B-F2	109.7
B-F2	1.356	F1-B-F3	110.7
B-F3	1.360	F1-B-F4	107.9
B-F4	1.410	F2-B-F3	110.9
C1-C2	1.394	F2-B-F4	109.6
C2-C3	1.380	F3-B-F4	108.0
C3-C4	1.393	C1-C2-C3	116.5
C4-C5	1.371	C2-C3-C4	120.5
C5-C6	1.393	C3-C4-C5	121.4
C6-C1	1.398	C4-C5-C6	120.8
C1-N	1.400	C5-C6-C1	115.9
N-C7	1.131	C6-C1-C2	124.9
C7-C8	1.434	C1-C6-C10	123.0
C2-C9	1.501	C1-C2-C9	121.5
C6-C10	1.490	C2-C1-N	117.1
		C6-C1-N	118.0
		C1-N-C7	177.4
		N-C7-C8	179.2

to bring this ion towards the other half ion through the mirror plane (*cf.* Fig. 1) indicating that the disorder may be dynamic even at temperatures below 100 K. The libration motion of the nitrilium ion is far less extreme, the largest r.m.s. amplitude being 3.1° about the C4-C8 direction in the molecule; corrections to the bond lengths in this ion are thus quite small.

DISCUSSION

Bond lengths and angles are given in Table 2; Figs. 1 and 2 show the structure of the ions,

thermal ellipsoids and bond lengths corrected for thermal motion. Carbon-hydrogen bond lengths were found in the range 0.77(5) to 1.03(4) Å with a mean value of 0.95 Å. Estimated standard deviations in distances and angles were calculated from the correlation matrix to be 0.003–0.004 Å and 0.2° , respectively, when not involving hydrogen atoms.

Tetrafluoroborate ion. Owing to the disorder, the structure of this ion is not well determined. The mean value of the B-F bond length is 1.38 Å (1.41 Å corrected for libration) with standard deviation from the mean of 0.02 Å. The F-B-F angles are found to be approximately tetrahedral.

N-(2,6-Dimethylphenyl)acetonitrilium ion. All atoms of the nitrilium ion except for two hydrogen atoms of each methyl group are coplanar by crystal symmetry requirements. Thermal parameters indicate that the ion is little affected by the disorder of the anion.

The carbon-carbon bond lengths in the dimethylphenyl part are normal. The bond angles in the ring deviate from 120° as expected in the presence of a very strongly electron-withdrawing substituent such as a nitrilium group, and the effect is of the same magnitude as that found in aryldiazonium ions. The internal angle at the carbon atom carrying the electropositive substituent is 124.9° as compared to the corresponding angle in benzenediazonium chloride of 124.8° ¹³ and in *p*-benzenediazonium sulfonate of 125.4° .¹⁴ The internal angles at the neighbouring carbon

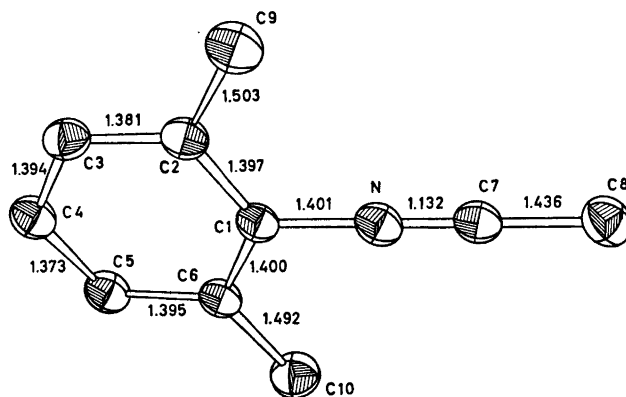


Fig. 2. Perspective view of the nitrilium ion not including hydrogen atoms. Distances (Å) are corrected for thermal libration.

atoms are correspondingly less than 120° , 116.2° in the nitrilium salt and 117.6 and 116.3° , respectively, in the diazonium salts. The internal angles at C3, C4 and C5 are only slightly larger than 120° . The methyl groups at C2 and C6 are not symmetrically arranged about the long axis of the molecule; the hydrogen atom bonded to C9 situated in the mirror plane is pointing away from the nitrilium group, whereas that bonded to C10 is pointing parallel to the C1–N bond. The latter hydrogen atom is thus situated fairly close to the nitrogen atom; repulsion between these atoms is probably responsible for a larger external angle C1–C6–C10 (123.0°) than C1–C2–C9 (121.5°) and for the asymmetry in external angles at C1.

The acetone nitrilium chain, C1–N–C7–C8, is almost linear and form *Ib* is thus the major contributor to the structure in the solid state as well as in solution.⁸ The N≡C7 bond length is found to be 1.13 \AA , the C1–N bond 1.40 \AA and the C7–C8 bond 1.44 \AA . However, in structure determinations by X-ray methods applying mainly low-angle data valence electrons may influence the results. One would expect the high electron density in the C–N triple bond to result in a measured bond distance shorter than the real internuclear separation. The high-angle data are more dependent on the inner-shell electrons and less on the valence electrons and may therefore be used to determine the nuclear positions more correctly.¹⁵ Least-squares refinement of the parameters of the heavy atoms using data with $\sin\theta/\lambda >$

0.45 \AA^{-1} (1200 reflections) gave the following bond lengths in the nitrilium chain: N≡C7 1.15 \AA ; C1–N 1.39 \AA , and C7–C8 1.43 \AA . Although the standard deviations in the bond lengths are slightly larger (0.005 \AA), we believe that the latter bond lengths are the more correct.

CNDO-calculations. In order to obtain an indication of the charge distribution along the nitrilium ionic chain, the CNDO method was employed to calculate the net charges on the atoms. A description of the standard version CNDO/2 is given in Ref. 16, which also gives the parameters needed in the calculations; the molecular geometry used was that found in the present low-temperature structure determination. Somewhat surprisingly the largest positive charge, $+0.25$, was found to be on C7. On the nitrogen atom, which classically, might be expected to carry the positive charge the calculated net charge was $+0.10$; the remaining positive charge was found to be distributed mainly among the methyl hydrogen atoms. The calculations were repeated with a crystal field simulated by placing four negative charges (F^-) in positions relative to the nitrilium ion corresponding to those of the BF_4^- ions in the crystal. This resulted in a net charge on C7 of $+0.36$, on the nitrogen atom of only $+0.05$ and a small increase in the positive charge on the hydrogen atoms nearest to the negative ions. The nitrilium ionic chain is clearly easily polarized, as expected for a triple bond.

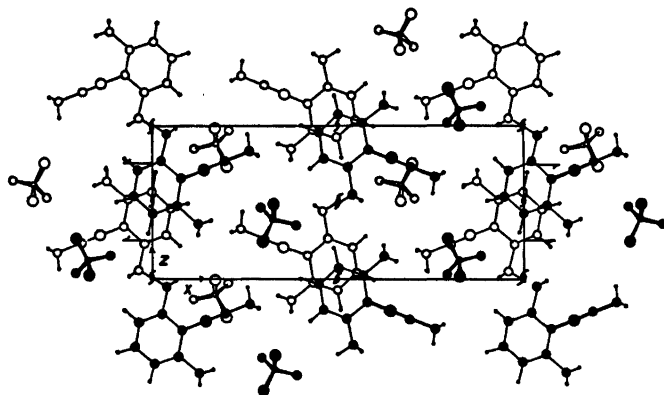


Fig. 3. The packing as seen along the *b*-axis. Filled circles are atoms of layer in $y = \frac{1}{4}$, open circles of layer in $y = \frac{3}{4}$.

Crystal packing. The crystals consist of nitrilium and tetrafluoroborate ions in layers parallel to the (010) plane in $y = \frac{1}{4}$ and $y = \frac{3}{4}$. The layers coincide with the crystallographic mirror planes; the layers are visualized in Fig. 3 as seen along the b axis.

Within each layer the nitrilium ions form chains along the a axis with van der Waals' contacts between phenyl hydrogen atoms in one ion and the hydrogen atoms of the C8 methyl group in another. Between the chains there are van der Waals' contacts between phenyl methyl groups. The tetrafluoroborate ions are situated in cavities formed between four nitrilium ions. This cavity seems to be too small to accommodate a tetrafluoroborate ion in the ordered situation in the mirror plane. The separation of the layers is $\frac{1}{2}b$, i.e. 3.39 Å corresponding to the normal packing distance between aromatic rings.

Each dimethylphenylacetone nitrilium ion is surrounded by six tetrafluoroborate ions with their boron atoms at the corners of a distorted octahedron. Four of these are situated in the same layer as the nitrilium ion, one in the layer above and one in the layer below. Similarly, each tetrafluoroborate ion is surrounded by eight nitrilium ions.

The acetone nitrilium part of the organic ion, N-C7-C8, which apparently carries most of the positive charge, is coordinated to four BF_4^- ions in a distorted tetrahedral arrangement; two of these are situated in the same mirror plane and the others above and below the nitrilium group in neighbouring mirror planes. The latter BF_4^- ions appear to have stronger interactions with the nitrilium moiety; C7-F and C8-F distances are in the range 2.87 to 3.08 Å and there are several short distances between fluorine and methyl hydrogen atoms. The separations between the nitrilium group and the tetrafluoroborate ions in the same layer are larger, probably for steric reasons. The interionic forces are mainly those between fluorine atoms and the C8 methyl group.

Comparison of the high and low temperature structures

Owing to the scarcity of data obtained at room temperature the bond distances and

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angles are not accurate enough for a discussion to be of interest, and no particular differences in ionic geometry would be expected. Some differences in the packing may be noted, however. As the cell volume decreases by 6.3 % when going from +18 to -169 °C, the packing is obviously denser at low temperatures. The decrease in cell parameters is 1.9, 3.6, and 0.9 % in the a , b , and c -axes, respectively. The large change in the b -axis reduces the inter-layer distance from 3.52 to 3.39 Å; this is reasonable since this separation is mainly determined by the comparatively weak forces between phenyl groups.

Although the separation of nitrilium ions also decreases within the layers when the compound is cooled, the C-F and N-F interionic distances show little variation due to changes in orientation of the BF_4^- ion. The equilibrium positions of the two half ions with a common position of the central boron atom seem to shift in the direction of an ordered situation. At room temperature the two fluorine atoms closest to the mirror plane are found 0.45 and 0.65 Å out of the plane, respectively. At low temperature the deviations from the plane have decreased to 0.25 and 0.40 Å, and one might expect that they coincide with the plane at even lower temperatures.

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