# 154. Interactions between Functional Groups

## Part II

## Structure of the 2-Dimethylaminobenzenediazonium Cation: Retention of Planarity Despite Excessive Steric Crowding

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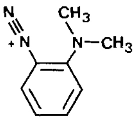
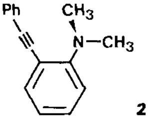
*Summary*

The crystal structure of 2-dimethylaminobenzenediazonium tetrafluoroborate has been determined at 183 K by X-ray diffraction. The cation is very nearly planar, the strong steric interaction between the *ortho*-groups being diminished by in-plane angular distortions.

The chemistry of multifunctional compounds can usually be understood in terms of the characteristic properties of the functional groups present with allowance for through-bond interactions. Through-space interactions have received much less attention and have been studied in detail only in one or two cases [1]. We have now determined the structure of the 2-dimethylaminobenzenediazonium cation **1** at 183 K to investigate the relative importance of through-bond and through-space interactions of the $-N(CH_3)_2$ and $-N{\equiv}N$ groups.



**1**



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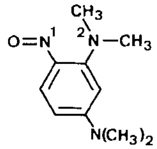

**3**

The structure of the cation is depicted in *Fig. 1a* with interatomic distances shown; bond angles are given in *Fig. 1b*. It is quite remarkable that the $Me_2N$ group retains planarity and is virtually coplanar with the benzene ring despite the steric pressure from the diazonium group. This repulsion is relieved almost exclusively by in-plane angular distortions rather than by displacements perpendicular to the aromatic plane. Thus N(1) and C(7) lie only 0.036 and 0.067 Å on opposite sides of this plane. The angular distortions consist of a severe splaying apart of the exocyclic bonds to the substituents, a widening of the C(2)–N(3)–C(7) angle by about 4.5° (with a concomitant compression of the C(7)–N(3)–C(8) angle to 114.9°), and a bending of the diazonium group at N(1) by 6°.

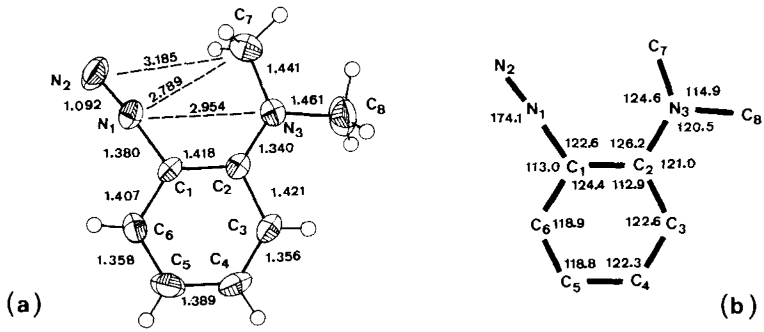

Fig. 1. a) *View of* **1** *with thermal vibration parameters drawn at the 50% level* [11], *and interatomic distances* (Å, e.s.d. *ca.* 0.005 Å, corrections for rigid-body thermal motion, *ca.* 0.006 Å, not included). Deviations (Å) from the plane of the benzene ring: N(1) 0.036, N(2) 0.078, N(3) – 0.053, C(1) 0.007, C(2) – 0.013, C(3) 0.010, C(4) 0.000, C(5) – 0.007, C(6) 0.004, C(7) – 0.067, C(8) – 0.101. b) *Bond angles* (°) (e.s.d. ≈ 0.4°).

The N(1)···C(7) distance of 2.79 Å is well within the sum of the standard [2] *van der Waals* radii (1.7 + 1.5 = 3.2 Å)[1]. The distance of N(1) from the two approximately equidistant methyl H atoms on C(7) is about 2.5 Å. However, the positions found for these H atoms are probably affected by orientational disorder of the methyl groups and thus not very reliable. For example, the distance between the two in-plane H atoms on C(7) and C(8) is calculated to be only 1.9 Å, which is improbably short.

The main factor responsible for the planarity of the cation is undoubtedly the strong through-bond interaction between the *ortho*-groups *via* the C(1)–C(2) bond. In contrast, the $Me_2N$ group in the tolane derivative **2** adopts pyramidal geometry [1]. Evidently, the –C≡CPh group is not a sufficiently strong $\pi$-acceptor to counterbalance the energy of steric repulsion between the groups in a coplanar arrangement. In the substituted nitrosobenzene **3** [6], the *ortho*-$NMe_2$ group is planar at the N atom, with angular distortions similar to those in **1**. However, the C–N(O) bond is splayed inwards instead of outwards and the *ortho*-N atoms are strongly displaced to opposite sides of the mean plane of the benzene ring: N(1) by 0.437 Å, N(2) by 0.205 Å. In this molecule outward splaying of the *ortho*-groups is opposed by (N)O···H repulsion.

In **1** the through-bond interaction between the *ortho*-substituents is manifested by the shortening of the exocyclic bonds: C(1)–N(1) is 1.380(5) Å (*cf.* 1.410–1.415 Å for the benzenediazonium cation [7]) and C(2)–N(3) is 1.340(5) Å [*cf.* 1.38(1) Å for *N,N*-dimethylanilines which have no strong electron-donating or -accepting substituents[2])]. The bond lengths and bond angles in the benzene ring deviate quite markedly from $D_{6h}$ symmetry: in particular, the bonds C(3)–C(4) and C(5)–C(6) are short [1.356(5) and 1.358(5) Å] and the angle at C(2) is remarkably small [112.9(4) °]. Together with the

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[1]) The radius appropriate for a diazonium $\alpha$-N atom is probably about 0.1 Å less than the standard value of 1.5 Å, judging from the contact distances observed in the crystal structures of benzenediazonium chloride [3] and 8-nitronaphthalenediazonium tetrafluoroborate [4]. This would be 0.3 Å smaller than the 1.7 Å radius proposed by *Bondi* for an N atom in a CN group [5].

[2]) Data obtained from the Cambridge Structural Database available from the Cambridge Crystallographic Data Centre, University Chemistry Laboratory, Cambridge, England.

shortening of the exocyclic bonds the pattern of bond lengths in the ring points to a palpable *ortho*-quinoid character of the cation.

Bond angles in substituted benzenes are usually reproduced rather well by summing the appropriate, angular deviation parameters for the groups present [8]. Even for deviations as large as in **1** the agreement between expected and observed angles is still reasonably satisfactory *(Table 1)*.

Table 1. *Observed and Calculated* [8] *Angles* (deg) *of the Benzene Ring in* **1**

| | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) |
|---|---|---|---|---|---|---|
| Observed | 124.4 | 112.9 | 122.6 | 122.3 | 118.8 | 118.9 |
| Calculated | 126.6 | 113.5 | 121.1 | 122.6 | 118.8 | 117.3 |

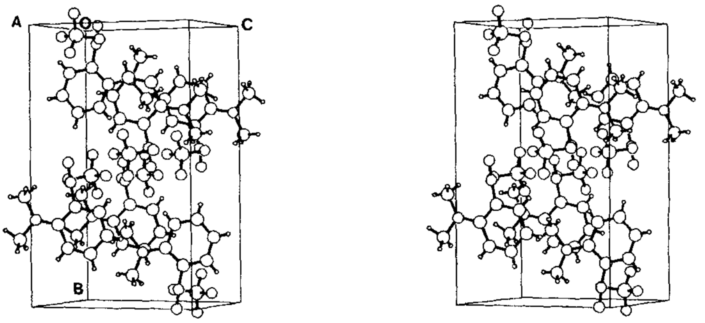

Fig. 2. *Stereoview* [12] *of the crystal structure viewed almost along the* a *axis*

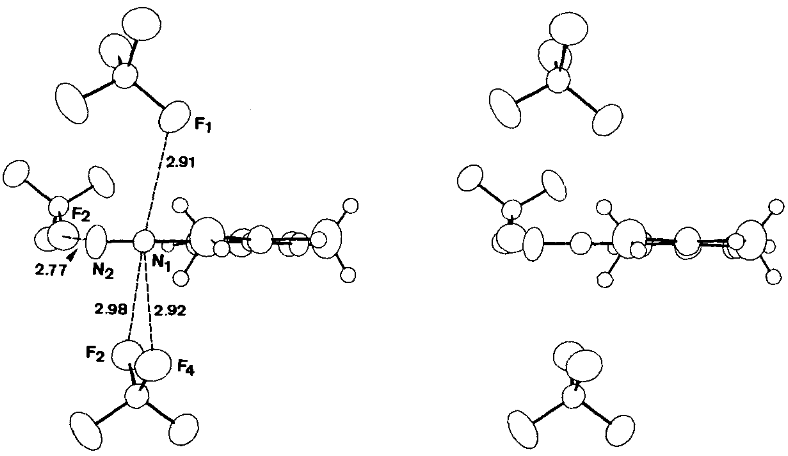

Fig. 3. *Stereoview of arrangement of* $BF_4^-$ *anions round a diazonium group*

**Packing.** – The planar cations lie almost perpendicular to the ***a*** axis, as shown in *Fig. 2*. Benzene rings of cations related by the [100] translation are interleaved by $Me_2N$ groups of cations related by the glideplanes. The diazonium groups are interposed between pairs of $BF_4^-$ anions in the $\pm$***a*** direction. Each diazonium group also makes

Table 2. *Positional and Vibrational Parameters for* **1** (standard deviations in parentheses). The Temperature Factor Expression is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hka^*b^*\ldots)]$ for non-H-atoms, $\exp[-8\pi^2U(\sin\theta/\lambda)^2]$ for H-atoms.

| Atom | $X$ | $Y$ | $Z$ | $U_{11}$ or $U$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | 0.3284(4) | 0.0599(2) | 0.1869(4) | 0.027(2) | 0.026(2) | 0.037(2) | −0.003(1) | 0.009(1) | −0.004(1) |
| N(2) | 0.3230(6) | −0.0083(2) | 0.1969(4) | 0.060(3) | 0.023(2) | 0.053(2) | −0.007(2) | 0.016(2) | −0.005(2) |
| N(3) | 0.3439(5) | 0.1911(2) | 0.4131(4) | 0.037(2) | 0.033(2) | 0.028(2) | −0.001(2) | 0.004(1) | −0.003(1) |
| C(1) | 0.3382(5) | 0.1449(2) | 0.1597(4) | 0.025(2) | 0.018(2) | 0.035(2) | −0.001(1) | 0.004(2) | 0.001(2) |
| C(2) | 0.3486(5) | 0.2061(2) | 0.2715(4) | 0.019(2) | 0.024(2) | 0.032(2) | 0.000(1) | 0.002(1) | −0.001(2) |
| C(3) | 0.3646(6) | 0.2893(2) | 0.2189(5) | 0.031(2) | 0.021(2) | 0.044(3) | −0.001(2) | 0.000(2) | −0.003(2) |
| C(4) | 0.3627(6) | 0.3071(3) | 0.0759(5) | 0.039(3) | 0.027(2) | 0.051(3) | −0.004(2) | 0.001(2) | 0.014(2) |
| C(5) | 0.3485(7) | 0.2450(3) | −0.0299(5) | 0.056(3) | 0.049(3) | 0.032(3) | −0.005(2) | 0.004(2) | 0.013(2) |
| C(6) | 0.3372(7) | 0.1635(3) | 0.0114(5) | 0.047(3) | 0.037(2) | 0.029(2) | −0.004(2) | 0.007(2) | −0.007(2) |
| C(7) | 0.3294(9) | 0.1089(4) | 0.4757(6) | 0.064(4) | 0.048(3) | 0.033(3) | −0.003(3) | 0.008(2) | 0.008(2) |
| C(8) | 0.351(1) | 0.2605(4) | 0.5168(6) | 0.068(4) | 0.055(4) | 0.042(3) | −0.006(3) | 0.014(3) | −0.019(3) |
| B(1) | 0.8228(7) | 0.0373(3) | 0.2304(5) | 0.031(2) | 0.029(2) | 0.036(2) | −0.002(2) | 0.004(2) | 0.003(2) |
| F(1) | 0.9490(4) | 0.1028(2) | 0.2378(3) | 0.050(2) | 0.046(2) | 0.066(2) | −0.014(1) | 0.006(1) | 0.004(1) |
| F(2) | 0.7101(4) | 0.0386(2) | 0.0986(3) | 0.058(2) | 0.064(2) | 0.046(2) | 0.003(2) | −0.006(1) | −0.011(1) |
| F(3) | 0.9117(5) | −0.0370(2) | 0.2524(4) | 0.076(2) | 0.043(2) | 0.098(3) | 0.026(2) | 0.014(2) | 0.012(2) |
| F(4) | 0.7069(4) | 0.0505(2) | 0.3390(3) | 0.048(2) | 0.066(2) | 0.052(2) | −0.004(1) | 0.012(1) | −0.006(1) |
| H(31) | 0.370(6) | 0.327(3) | 0.280(4) | 0.03(1) | | | | | |
| H(41) | 0.364(7) | 0.359(3) | 0.056(5) | 0.04(1) | | | | | |
| H(51) | 0.344(7) | 0.256(3) | −0.119(6) | 0.06(2) | | | | | |
| H(61) | 0.346(6) | 0.123(3) | −0.045(5) | 0.04(1) | | | | | |
| H(71) | 0.441(5) | 0.077(2) | 0.455(4) | 0.015(9) | | | | | |
| H(72) | 0.236(7) | 0.081(3) | 0.433(6) | 0.05(2) | | | | | |
| H(73) | 0.36(1) | 0.111(5) | 0.579(9) | 0.13(3) | | | | | |
| H(81) | 0.259(9) | 0.299(4) | 0.497(7) | 0.09(2) | | | | | |
| H(82) | 0.459(9) | 0.290(4) | 0.517(6) | 0.08(2) | | | | | |
| H(83) | 0.35(1) | 0.227(6) | 0.61(1) | 0.18(4) | | | | | |

contact with a third $BF_4^-$ anion approximately in the *c* direction and roughly in the molecular plane, as shown in *Fig. 3*. There are four N···F distances less than 3 Å, the shortest (2.77 Å) being the one between the outer nitrogen N(2) and F(2) of the anion in the molecular plane. There is also a relatively short F···H contact distance of 2.34 Å between F(4) and the methyl hydrogen H(71).

**Thermal Motion.** – The atomic vibration parameters for **1** are not as reliable as we would wish because of disorder (see *Exper. Part*). The rigid-body libration tensor of the cation is reasonably isotropic with eigenvalues in the range 13–20 deg$^2$ at 183 K. Calculations including the effect of an internal libration of the $Me_2N$ group about the C(2)–N(3) bond did not lead to significantly improved agreement between observed and calculated vibration parameters.

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## Experimental Part

*Preparation of 2-Dimethylaminobenzenediazonium Tetrafluoroborate.* Diazotisation of *N,N*-dimethylbenzene-1,2-diamine with $NaNO_2$ in aq. fluoroboric acid did not produce crystals as reported [9], so the solution was neutralized with $NaHCO_3$ and evaporated to dryness at r.t. The residue was dissolved in MeCN and the $NaBF_4$ precipitated by addition of $Et_2O$. The remaining solution was diluted with more $Et_2O$ and cooled to −30° to give an orange precipitate of 2-dimethylaminobenzenediazonium tetrafluoroborate. A few crystals, m.p. 88–89° ([9]: 85–86°), suitable for X-ray analysis were grown from a $MeCN/Et_2O$ solution at −30°.

*Determination of the Crystal Structure of 2-Dimethylaminobenzenediazonium Tetrafluoroborate.* $C_8H_{10}N_3 \cdot BF_4$, $M = 235.0$. Orange needles, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 7.198(3)$, $b = 15.922(8)$, $c = 9.278(3)$ Å, $\beta = 96.96(4)°$ at 183 K ($a = 7.256(3)$, $b = 15.914(4)$, $c = 9.331(3)$ Å, $\beta = 96.84(3)°$ at 253 K).

Intensity measurements were made at 183 K using an *Enraf Nonius CAD4* diffractometer equipped with a graphite monochromator (Mo$K\alpha$, $\lambda = 0.71069$ Å) and a cooling device. The structure was solved by direct methods and refined [10] using the 1549 measured reflections with $I \geq 3\sigma\,(I)$ and $\theta \leq 27°$. H atoms were located from a difference *Fourier* synthesis and assigned isotropic vibration parameters (other atoms anisotropic). A difference map calculated towards the end of the refinement showed four peaks of 0.5–0.7 e $A^{-3}$ at distances of 1.2–1.6 Å from the B atom. The positions of these 'shadow' peaks lay close to the vertices of the tetrahedron obtained by inverting the $BF_4^-$ tetrahedron through the B atom. Attempts to refine the parameters of the additional peaks in terms of a disorder model were not successful so the refinement was terminated at this point ($R = 0.066$, unit weights). Atomic parameters are listed in *Table 2*.

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