88. Interactions between Functional Groups

Part IV

The Responses of Four Diazonium Groups to Adjacent Electron-Rich Atoms in Peri-Substituted Naphthalene and Quinoline Derivatives

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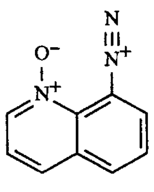
Four peri-substituted naphthalene-1-diazonium cations all show short attractive interactions between an electron-rich atom of the peri-substituent and the α-N-atom of the diazonium group. These are interpreted as models for incipient nucleophilic attack on a N≡N bond. The diazonium group is a better acceptor of electron density 'through space' than the NO_2 group, which parallels their relative 'through-σ-bond' inductive effects.

Introduction. – The diazonium group is the most electron-deficient of the common functional groups encountered in organic compounds and exerts very strong inductive and mesomeric effects [1]. Not surprisingly, aromatic diazonium salts undergo nucleophilic addition reactions at the β-N-atom with anions such as thiolate and cyanide to yield (*Z*)- and (*E*)-1,2-diazenes [2]. In contrast, addition to the α-N-atom would produce unstable 1,1-diazenes which decompose readily with loss of N_2 gas [3]. The optimal reaction coordinate for attack of a nucleophile on a triple bond has been a subject of debate [4] [5]. Indications of the preferred approach geometry may be detectable in the structures of molecules in which prototypes of the reacting groups can interact through space, as has been demonstrated for nucleophile/C=O group interactions [6] [7]. With this in mind, we have measured the low-temperature crystal structures of four 8-substituted naphthalene-1-diazonium cations **1**–**4** (as their tetrafluoroborate salts), in which an electron-rich atom (O, S, or N) belonging to the peri-substituent interacts with the electrophilic N≡N bond.



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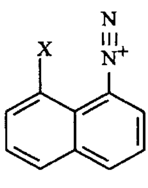

2 X = MeS
3 $X = Me_2N$
4 $X = NO_2$

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Discussion. – All four cations **1**–**4** exhibit similar attractive interactions between an electron-rich atom (**1**, **4**:O, **2**:S, **3**:N) and the α-N-atom of the diazonium group. Structural details are summarized in *Table 1*. There are four common features: *i*) The distance (*a*) between the interacting atoms is less than the sum of the appropriate *van der Waals* radii, *ii*) the C—N≡N group is bent at the α-N-atom by *ca.* 10° (180° – *ν*) such that the α-N-atom is displaced from the C···N(*β*) line towards the electron-rich atom, *iii*) the nucleophile···N(α)≡N(*β*) angle (*μ*) is greater than 90°, and *iv*) the substituents are displaced slightly to opposite sides of the naphthalene ring's best plane (*Table 2*). In **1** and **3**, where the electron-rich atom is directly attached to the ring system, the in-plane displacements of the substituents are in the same sense, with the diazonium group bent outwards and the substituent bent inwards. These displacements increase the *μ* angles to 104.4(2) and 105(1)°, respectively. Outward in-plane displacement for the substituent and inward displacement of the diazonium group would have reduced this angle. Although the outward displacement may be disfavoured for **3** by steric interactions of the *N*—Me groups with the *ortho*-H-atom, there can be no such hindrance effect for **1**, in which the electron-rich atom is unsubstituted. Indeed, this structure provides a very strong indication that the favoured nucleophile···N(α)≡N(*β*) angle *μ* is greater than 90°, and at least 104°. Similar results have been obtained for approach of a nucleophile to a CN group [8].

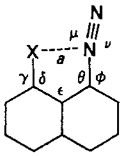

Table 1. *Details of Intramolecular Interactions.* Distances in Å, angles in °.

	X	*a*	*μ*	*ν*	*γ*	*δ*	*ε*	*θ*	*φ*
1	O	2.443(2)	104.4(1)	169.6(1)	121.9(1)	118.4(1)	120.7(1)	120.5(1)	116.5(1)
2	MeS	2.938(5)	99.8(2)	170.1(2)	118.9(2)	122.5(2)	127.7(2)	121.7(2)	112.4(2)
3	Me_2N	2.54(1)	105(1)	167(1)	123(1)	117(1)	125(1)	121(1)	113(1)
4	NO_2	2.500(2)	93.3(1)	171.4(1)	115.5(1)	122.0(1)	130.5(1)	123.5(1)	111.4(1)

Table 2. *Deviations* [Å × 10^3] *of Atoms from the Plane Defined by the C- and N-Atoms of the Naphthalene Ring System*

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	N(8) orC(8)	C(9)	C(10)
1	34	10	–31	–9	15	15	–15	–32	6	2
2	37	16	–18	–22	12	36	–15	–37	–3	–7
3	11	65	–36	–52	66	52	–83	12	–8	–28
4	41	69	–13	–54	23	71	6	–69	–39	–34

	N(1)	N(2)	N(3)	S(1)	C(11)	C(12)	O(1)	O(2)
1	192	359	–	–	–	–	–94	–
2	196	358	–	–232	1284	–	–	–
3	66	82	–33	–	–1390	849	–	–
4	177	321	–271	–	–	–	–934	191

In cation **2**, the nucleophilic S-atom is also directly attached to the ring system, but the larger size of the S-atom is responsible for the substituents being splayed apart, although the S···N(α) distance is still within the sum of *van der Waals* radii. However, the splaying is asymmetric, with the diazonium group splayed more outwards than the S–Me group leading to a μ angle of 99.8(2)°. (This angle would have been reduced if the S–Me group were splayed more outwards than the diazonium group.) The smaller μ angle compared with **1** and **3** is a consequence of the greater length of the C(8)–S(1) bond compared with the corresponding N–O and C–N bonds in **1** and **3**. The substituents in the overcrowded cation **4** are also splayed apart. The plane of the NO_2 group is rotated by 33° to the aromatic plane so that the distance between a nitro O-atom and the diazonium α-N-atom becomes 2.500(2) Å. The O···N≡N angle is 93.3(1)°. Similar interactions between diazonium groups and carboxylate or carboxylic groups have been reported by *Gougoutas* [9–12].

In summary, the electron-rich centre in each of the four cations interacts with the α-N- rather than the β-N-atom of the diazonium group. The latter would have led to the geometry indicated in *Fig. 1A*, the former to that in *Fig. 1B*, which is observed in all four structures. Although the products of α-addition (and the transition states leading to them) are of higher energy than those of β-addition²), the stereoelectronic requirements for addition to either *N*-atom should be similar in the early stages of the reaction. Our results are consistent with the idea that the favoured approach direction of the nucleophile is such as to optimize the overlap between the incoming lone-pair electrons and the anti-bonding π^* orbital of the N≡N bond. Recent claims [13] that interactions between diazonium α-N-atoms and centres of high electron density are repulsive rather than attractive must be regarded with reserve.

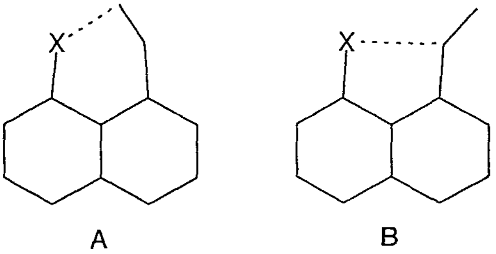

Fig. 1. *Patterns of molecular distortions for interaction of nucleophilic centre X with* A) *the β-N-atom,* B) *the α-N-atom of the diazonium group*

The diazonium group is a remarkable functional group which exerts powerful 'through-bond' and 'through-space' electronic effects. The size of the endocyclic *ipso*-angle in monosubstituted benzene derivatives has been shown to be directly correlated with the inductive effect of the substituent [14] [15], a larger angle corresponding to a larger negative inductive effect. Indeed, the diazonium group produces the largest *ipso*-angles, 126.0(2)° in benzenediazonium tetrafluoroborate [16] and 125.5(7)° in its 4-Br

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²) The heat of formation of a 1,1-diazene has been estimated to be *ca.* 20 kcal·mol⁻¹ higher than a 1,2-diazene [3].

derivative [17]. In **1**–**4**, these angles lie in the range 122–127°. Furthermore, the O···N(α) distance of 2.500 Å in **4** is markedly shorter than the O···N distances in 1,8-dinitronaphthalene (2.664(3), 2.705(3) Å) [18], suggesting that the α-N-atom of a diazonium group is also a stronger 'through-space' acceptor of electron density than the N-atom of a NO_2 group, as well as being a stronger 'through-σ-bond' acceptor.

Besides taking part in addition reactions, the diazonium group is readily substituted. Although there have been many investigations into the mechanisms of these processes [19], the possibility of initial addition to α-N-atom, followed by elimination of N_2, does not seem to have received serious consideration. The preference of electron-rich atoms to coordinate the α-N- rather than the β-N-atom may be general, as illustrated by the coordination of the crown ether 21-C-7 to the 4-methoxybenzene-1-diazonium cation [20].

Structure of **1**·BF_4 *at 95 K* [21]. The structure of the cation is shown in *Fig. 2*, molecular geometry in *Fig. 3*. The BF_4^- counterion is well ordered. Corrections to bond lengths for rigid-body motion are ≤ 0.002 Å [22]. The main source of inaccuracy is likely

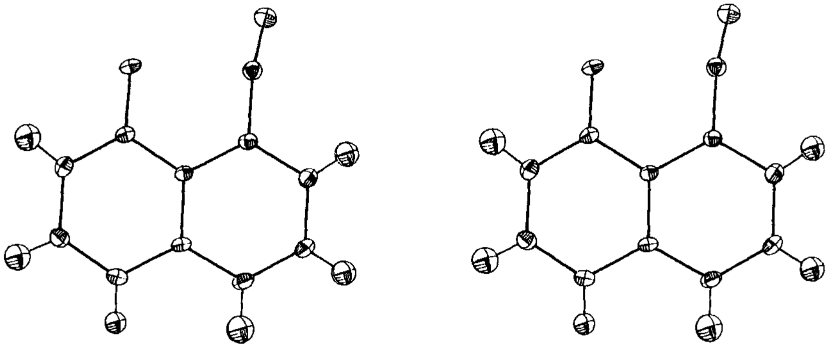

Fig. 2. *Stereoview of* **1** *showing* Gaussian *probability ellipsoids at 50% probability level* [23]

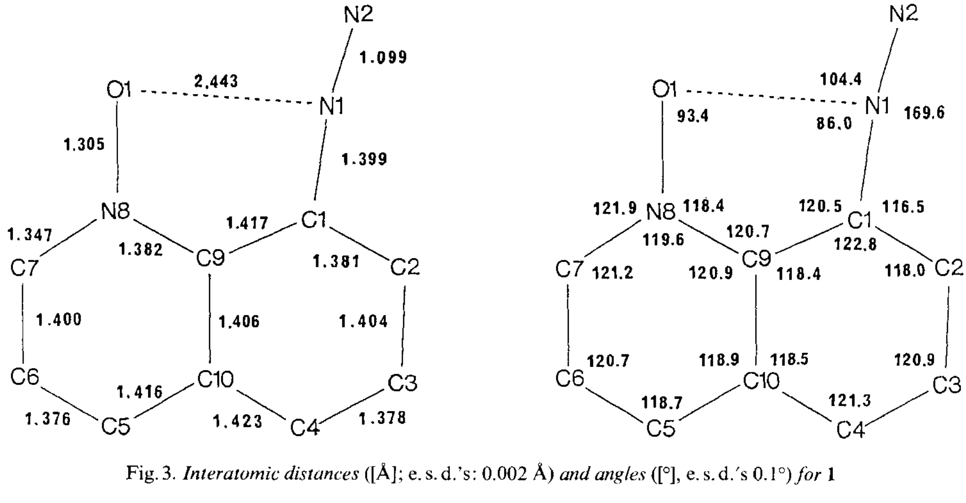

Fig. 3. *Interatomic distances* ([Å]; e.s.d.'s: 0.002 Å) *and angles* ([°], e.s.d.'s 0.1°) *for* **1**

to be in the positions and displacement parameters of the diazonium N-atoms, due to the limitations of the spherical-atom formalism in the presence of the severe asymmetry in electron-density distributions about these atoms. Both N-atoms are likely to be displaced from their true positions towards the centre of the $N{\equiv}N$-bond electron density, leading to a too short N,N distance. Indeed, final difference electron-density maps are almost featureless in the $C{-}N{\equiv}N$ region, while bonding electron-density peaks appear between all pairs of bonding atoms in the ring system.

Structure of **2**$\cdot$*BF_4 at 213 K.* A stereoview of **2** is shown in *Fig. 4*, molecular geometry in *Fig. 5*. The torsion angles C(11)–S(1)–C(8)–C(7) and C(11)–S(1)–C(8)–C(9) are −65° and +120°, respectively. This means that the Me group is twisted well out of the aromatic plane. Indeed, if the S valence electrons are described in terms of tetrahedrally disposed sp^3 orbitals, then the S–Me group is oriented such that a lone pair lies almost in the aromatic plane and directed towards the diazonium group. If the Me group lay in the

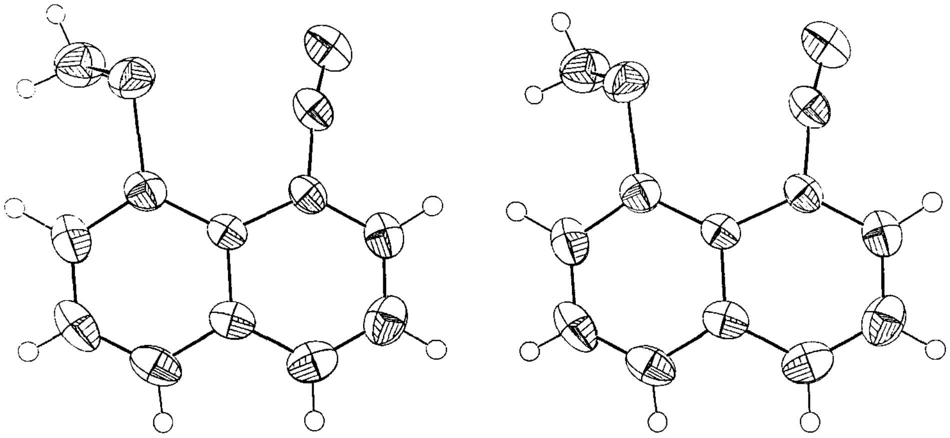

Fig. 4. *Stereoview of* **2** *showing* Gaussian *probability ellipsoids at the 50% probability level* [23]

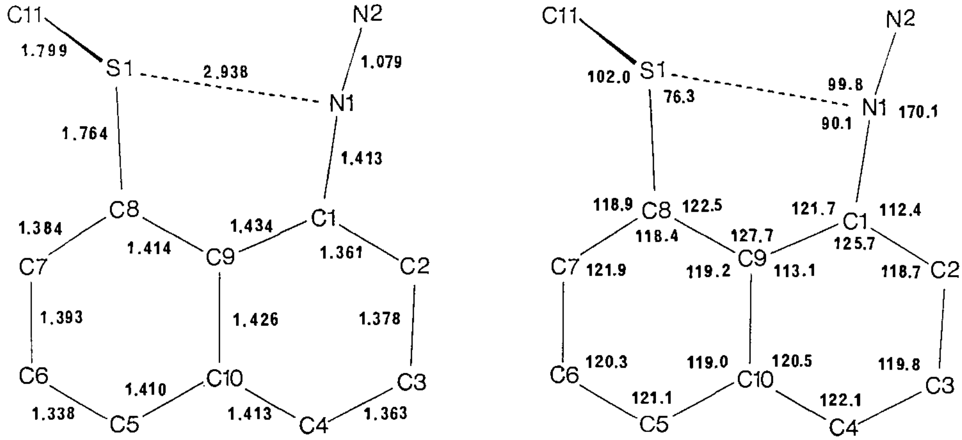

Fig. 5. *Interatomic distances* ([Å]; e.s.d.'s: 0.005–0.007 Å) *and angles* ([°]; e.s.d.'s: 0.2–0.4°) *for* **2**

plane of the aromatic ring (and directed away from the diazonium group), there would be a very short contact to the *ortho*-H atom ($H_3C \cdots H$ *ca.* 2.25 Å). The *Cambridge Structural Database* contains data for only three (methylthio)benzene derivatives unsubstituted in the *ortho*-positions [24] [25]. In two cases, the Me group is accommodated in the aromatic plane but the MeS group is displaced away from the *ortho*-H-atom. Nevertheless, the tendency for the Me group to lie in the aromatic plane appears not as strong as it is for methoxybenzenes. This contrast is clearly seen when the search is widened by allowing the Me group to carry a substituent.

The diazonium group is bent by 9.9(1)° at the α-N-atom. The peri-groups are splayed apart in the aromatic plane, but the $S \cdots N(\alpha)$ distance of 2.938(5) Å is still well within the sum of *van der Waals* radii (3.3 Å) for these atoms [27]. The C(8)–S(1) bond is splayed out rather less (by 1.8°) than the C(1)–N(1) bond (by 4.7°). This reduces steric repulsion between the Me group and the *ortho*-H-atom and also helps to make the $S(1) \cdots N(1){-}N(2)$ angle obtuse.

Structure of **3**·BF_4 *at 153 K.* A stereoview of this cation is shown in *Fig. 6*. It is clear that some of the atomic displacement parameters (ADP's) are elongated in directions which cannot be accounted for by rigid body motion. We believe that this structure may be partially disordered (see below). Some geometrical parameters derived from the average atomic coordinates are given in *Fig. 7*. The Me_2N group is oriented so as to direct its lone pair of electrons approximately towards the diazonium group. The $Me_2N \cdots N(\alpha)$ distance is quite short (2.54(1) Å), and the diazonium group is bent by *ca.* 13° in a similar way to that seen in **1** and **2**. It is typical of this family of structures that the two substituents are displaced to opposite sides of the aromatic plane. Disorder in this crystal structure may arise from some cation stacks having the opposite pattern of

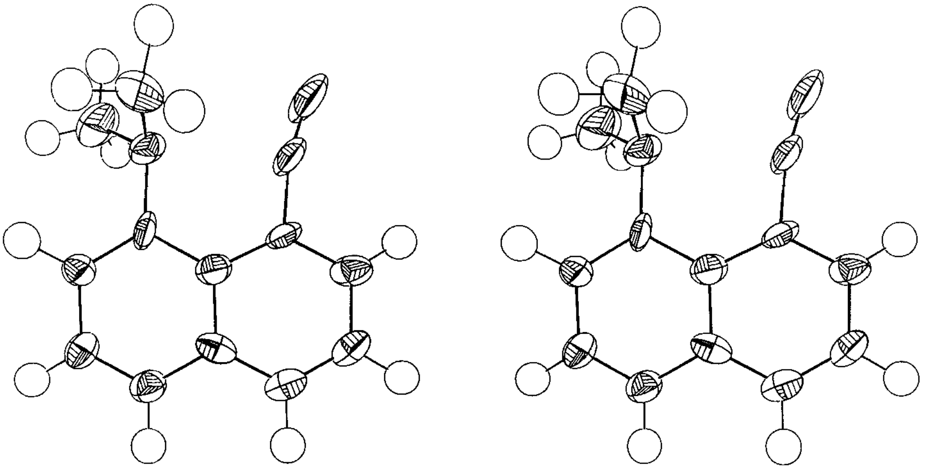

Fig. 6. *Stereoview of the averaged structure of* **3** *with* Gaussian *probability ellipsoids drawn at the 50% probability level* [23]. The large components of the substituent atoms' ellipsoids perpendicular to the molecular plane are due to disorder in the packing of the cations.

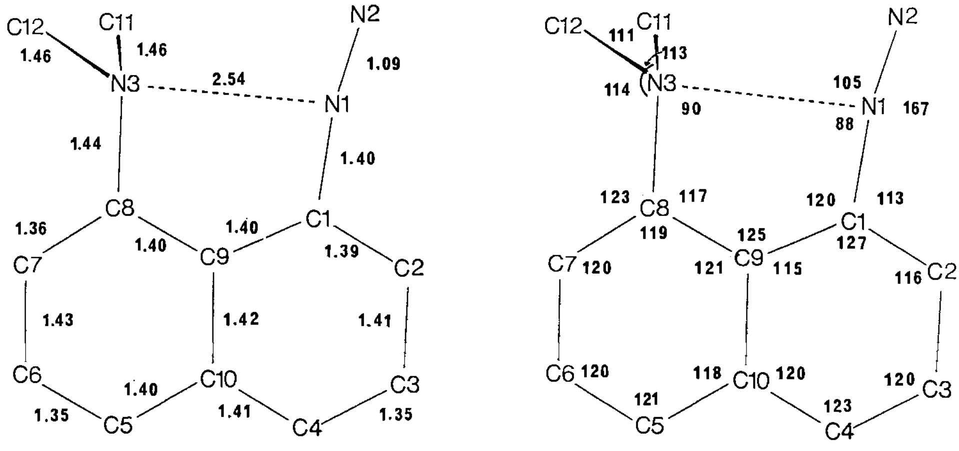

Fig. 7. *Interatomic distances* ([Å]; e.s.d.'s: 0.01–0.02 Å) *and angles* ([°]; e.s.d.'s 1°) *for the averaged structure of* **3**

out-of-plane displacements to the majority of stacks. (See crystal packing; neighbours within a stack are related by a 2_1 axis parallel to the stacking axis.) Such disorder would have the effect of reducing the apparent (average) out-of-plane displacements, and it can be seen that these displacements are smaller than those observed in **1** and **2** (*Table 2*). Our structure refinements in the space group $Pna2_1$ lead to atomic z coordinates that are within a standard deviation or so of $z = 0.75$ for all the heavy atoms except F(3) and F(4), which are related by reflection across this plane, and the two Me C-atoms, which are not. Thus, apart from the two Me groups, the atomic arrangement fits the higher, centrosymmetric space group *Pnam*, which raises the question whether this is indeed the correct space group. We believe that this is not the case. Attempts to refine the structure in the higher space group did not converge well and led to physically unreasonable displacement parameters (negative eigenvalues). It is more likely that the crystal structure is disordered. The molecules are arranged in stacks parallel to the c axis. In the lower space group, this is a polar axis. Disorder in the crystal structure could arise from some cation stacks having the opposite pattern of out-of-plane displacements to the majority of stacks. Such disorder would lead to artificially large atomic displacement parameters in the c direction, and indeed, the U_{33} parameters of the Me C-atoms C(11) and C(12) and of the β-N-atom of the diazonium group are much larger than those of the other atoms in the cation.

The *Pnam* space group would correspond to complete disorder, *i.e.* to 1:1 proportion for the two kinds of stacks with opposite polarity, whereas 'partial disorder' corresponds to unequal proportions. We believe that the actual crystal structure corresponds more closely to the latter.

Structure of **4**$\cdot$*BF*$_4$ *at 110 K.* A stereoview of cation **4** and the nearest BF_4 anion is shown in *Fig. 8*. Interatomic distances and angles are given in *Fig. 9*. The underestimation of the bond lengths in the cation due to molecular motion is here quite small, only *ca.* 0.002 Å. However, although the BF_4^- anion appears to be well-ordered, the reductions in its bond lengths due to molecular motion are much larger, *ca.* 0.01–0.03 Å [22]. The

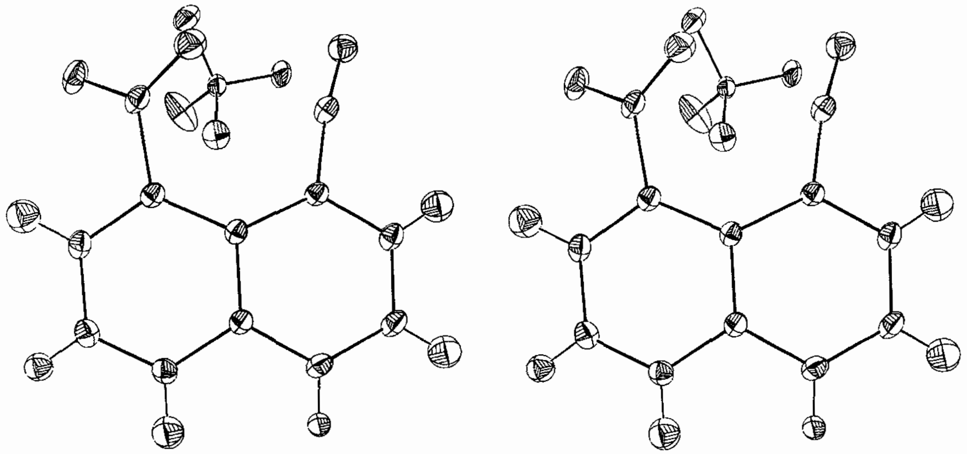

Fig. 8. *Stereoview of the cation* **4** *and the neighbouring BF_4 ion. Gaussian* probability ellipsoids are drawn at the 50% probability level [23].

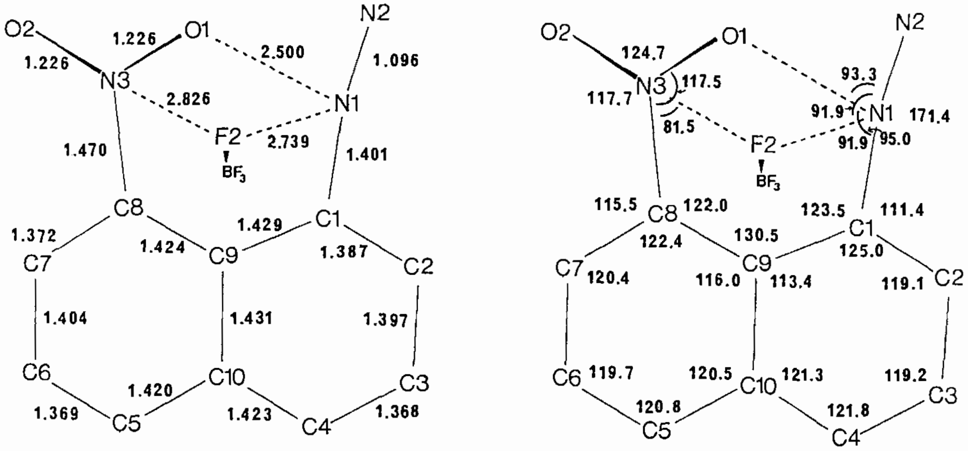

Fig. 9. *Interatomic distances* ([Å]; e. s. d.'s: 0.002–0.003 Å) *and angles* ([°]; e. s. d.'s: 0.1–0.2°) *for* **4** *and its interaction with the F-atom of neighbouring BF_4 ion*

peri-substituents are splayed apart and the plane of the NO_2 group lies 33° out of the aromatic plane so that one NO_2 O-atom makes a close approach to the diazonium α-N-atom. This interaction does not induce any significant asymmetry in the N–O bond lengths.

From *Figs. 8* and *9*, it is clear that a F-atom belonging to a BF_4^- anion lies close to both the diazonium α-N-atom and the NO_2 N-atom. The N(α)···F distance is 2.739(2) Å, somewhat longer than the intramolecular N(α)···O contact. However, the F-atom appears to have a weak attractive effect on N(α), since this atom is displaced from the plane defined by atoms C(1), N(2), and O(1) by 0.021 Å towards the F-atom. The same F-atom lies 2.826(2) Å from the NO_2 N-atom, and the NO_2 group is slightly pyramidalised such that its N-atom deviates from the plane defined by its three neighbours by

Table 3. *Bond Lengths* [Å] *for* BF_4^- *Anions*

$1 \cdot BF_4$	Uncorr.	1.400(2)	1.391(2)	1.399(2)	1.395(2)
	Corr.	1.411	1.402	1.408	1.405
$4 \cdot BF_4$	Uncorr.	1.388(2)	1.404(2)	1.370(3)	1.392(2)
	Corr.	1.402	1.423	1.396	1.418

0.019 Å towards the F-atom. (Small pyramidalities have been observed before for NO_2 N-atoms adjacent to electron-rich atoms [27].) It is significant that the corresponding B–F distance is the longest B–F bond in the anion (*Table 3*).

Since this crystal structure analysis is reasonably accurate, we have compared the molecular geometry of the ring system with that of naphthalene itself [28]. The amounts by which the bond lengths and angles of **4** differ from those of naphthalene are given in *Fig. 10*. Benzene-ring substituents with strong inductive effects are known to produce widening of the *ipso*-angle and reductions of the *ortho*-angles [14] [15]. These features are evident in **4**, where the angles at the fusion of the two rings are more severely reduced than the other pair of *ortho*-angles. Apparent changes in bond lengths can only be deemed reliable when the molecular motions are very small, a criterion fulfilled in this case, since the structures of naphthalene and **4** were measured near to 100 K. Furthermore, in **4** we can directly compare the influences of the NO_2 and diazonium groups. The diazonium group appears to induce increases in the *a* bonds while the NO_2 group induces very small decreases. These effects are smaller for the bonds directed towards the ring fusion. The diazonium group decreases the *b* bond more than the NO_2 group, while the *c* bonds are altered by similar amounts.

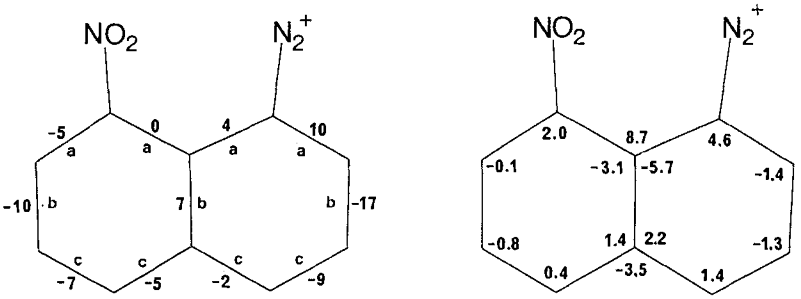

Fig. 10. *The changes in* a) *bond lengths* [A] *and* b) *bond angles* [°] *on substitution of naphthalene with a 1-diazonium group and a 8-*NO_2 *group*

Tetrafluoroborate Ions. We limit our discussion to $1 \cdot BF_4$ and $4 \cdot BF_4$ which were measured at temperatures ≤ 110 K. Thermal motion analyses of the BF_4 ions with computer program THMV [22] show that in both cases the mean-square vibrational amplitudes of the B-atoms along the B–F bonds are larger than those of the F-atoms in these directions (by 0.0010 – 0.0027 $Å^2$). This may be attributable to internal vibrations of T_2 symmetry. Rigid-body libration tensors for the anions have eigenvalues: $1 \cdot BF_4$: 35(6), 22(5), and 16(4) deg^2, $4 \cdot BF_4$: 103(10), 25(5), and 19(4) deg^2. Corrections to B–F bond lengths for rigid-body motion lie in the range 0.009–0.026 Å (*Table 3*).

Crystal Packings. The crystal packings of the BF_4 salts of **1**–**4** are shown in *Figs. 11–14*. For the first three structures, the cations are stacked along the shortest crystal axis. Neighbours within a stack are related by a centre of symmetry (**1** · BF_2 and **2** · BF_4) or a 2_1 axis (**3** · BF_4), and are oriented so that the substituents are directed to the outsides of the stacks. BF_4^- anions are located between diazonium groups related by a unit cell transla-

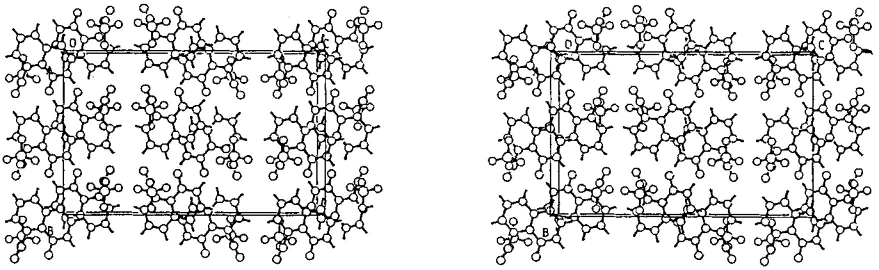

Fig. 11. *Crystal packing of* **1** · BF_4 *viewed down the [100] axis* [32]

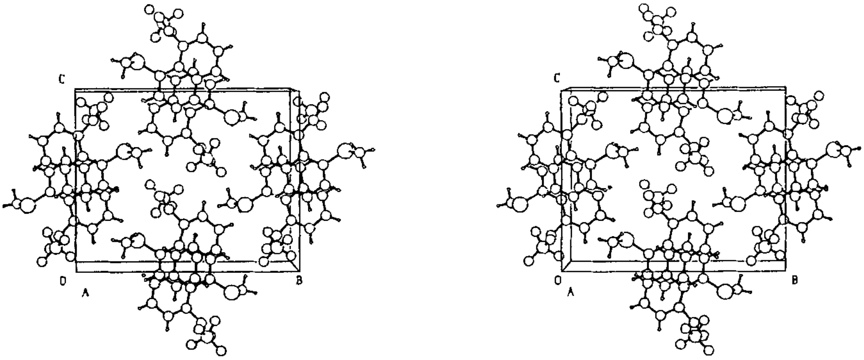

Fig. 12. *Crystal packing of* **2** · BF_4 *viewed down the [100] axis* [32]

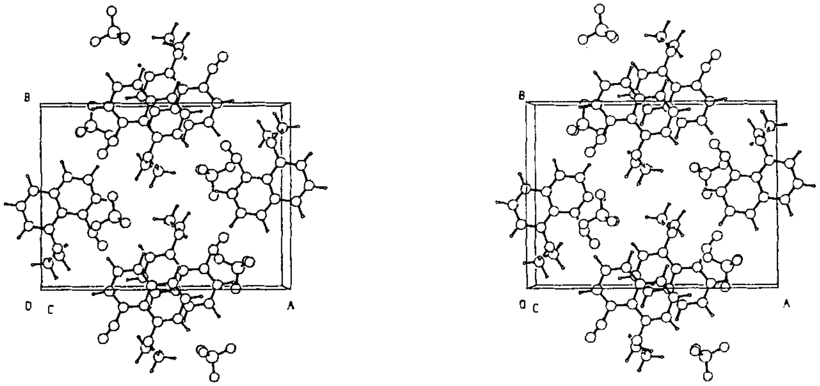

Fig. 13. *Crystal packing of* **3** · BF_4 *viewed down the [001] axis* [32]

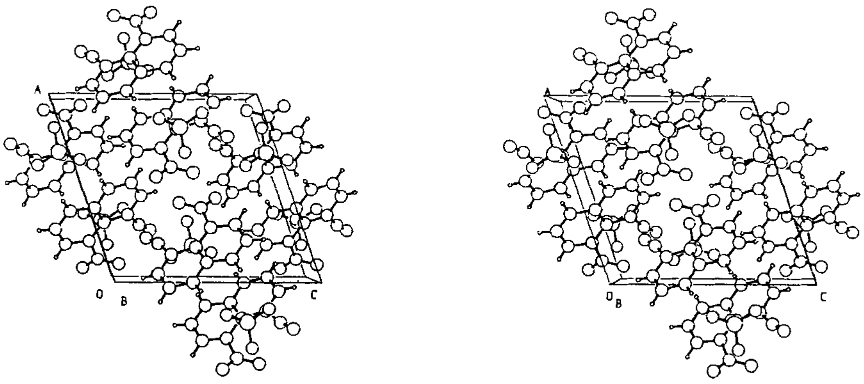

Fig. 14. *Crystal packing of* **4** · *BF_4 viewed down the [010] axis* [32]

tion along the stacking axis. The packing is more compact for **1** · BF_4 than for **2** · BF_4 and **3** · BF_4, since the cation **1** does not include atoms that lie far from the aromatic plane. In **4** · BF_4, the packing mode is quite different, since the anion makes attractive interactions with both peri-substituents. Cations and associated anions are packed into centrosymmetrically related pairs, but these are not stacked as for the other salts. Five other crystal structure of aryldiazonium tetrafluoroborates were found in the *Cambridge Structural Database* (4-bromo- [17], 4-morpholino- [29], 4-nitro- [30], 2-(dimethylamino)- [31], and unsubstituted [16] benzenediazoniums). Only the 2-(dimethylamino) structure has a stacking arrangement similar to that in **1**–**3** · BF_4, the planar Me_2N moiety adopting a similar orientation to the naphthalene ring, though neighbours within a stack are here related by glide planes.

The *Schiemann* reaction, the conversion of aryldiazonium tetrafluoroborates to the corresponding aryl fluorides, takes place on heating the solid salts or their solutions [33]. In solution, kinetic measurements indicate that dediazoniation precedes nucleophilic attack by BF_4^- and proceeds by two mechanisms, one leading to phenyl cations, the other to a $C_6H_5^+/N_2$ tight molecule-ion pair [34]. Little is known about the mechanism of the solid-state reactions. The ubiquitous presence of BF_4^- anions adjacent to the diazonium groups in the solid salts suggests the possibility that the transition state may involve partial $N(\alpha)\cdots F$ bonding. The shortest $N\cdots F$ contact in this series is in **4** · BF_4: $N(\alpha)\cdots F$ 2.739(2) Å.

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Experimental Part

Syntheses. Quinoline-8-diazonium-1-oxide Tetrafluoroborate (**1**·BF_4). 8-Aminoquinoline-1-oxide (100 mg), prepared from 8-nitroquinoline as described in [35], was dissolved in EtOH (4 ml) stirred and cooled to –5°. HBF_4 (50% aq., 0.14 ml) was added to the stirred soln. to give a yellow precipitate, followed by dropwise addition of isopentyl nitrite (20% in EtOH, 0.7 ml). After 3 h at –5°, a new dark orange precipitate was filtered off and recrystallised from $MeCN/Et_2O$ to give **1**·BF_4 (45 mg, 26%). M.p. 163°. IR (nujol): 2260.

8-(Methylthio)-1-naphthalenediazonium Tetrafluoroborate (**2**·BF_4). Commercial 2*H*-naphtho[1,8-*cd*]isothiazole-1,1-dioxide was purified by dissolving in Et_2O, filtering off a black solid, evaporating the filtrate and recrystallising the residue from toluene. The purified material was reduced to 8-amino-1-naphthalenethiol with $LiAlH_4$ in THF by modification of the procedure described in [36] (the acidified reaction mixture must be neutralised before extracting the product with Et_2O). The product was obtained as an orange solid (74%; m.p. 95–97° ([36]: 75–76°)) and stored under Ar.

A soln. of 8-aminonaphthalene-1-thiol (4.00 g, 22.9 mmol) in THF (70 ml) was cooled to –78°, and a 1.6M soln. of Bu*Li* in hexane (14.2 ml) added over 10 min. After stirring for 30 min at –78°, the resulting dark red soln. was treated with MeI (1.5 ml, 24.2 mmol), allowed to warm up slowly to r.t. and then refluxed for 1 h. The mixture was extracted with a mixture of brine (30 ml) and Et_2O (50 ml). The org. layer was extracted with brine and dried ($MgSO_4$). Filtration and evaporation yielded a mixture of 8-(methylthio)-1-naphthaleneamine and 1-(methylamino)-8-(methylthio)naphthalene which were separated by chromatography over basic alumina (4%, deactivated). After petroleum ether (40–60°) had eluted the dimethylated material, the required mono-methyl compound was eluted with petroleum ether/Et_2O 96:4 to furnish an oil (1.11 g, 26%) which crystallised after *Kugelrohr* distillation. M.p. 35–36°. B.p. 101°/0.001 Torr. IR (CCl_4): 3460*m*, 3335*m*. ^{1}H-NMR ($CDCl_3$): 2.44 (*s*, CH_3); 5.72 (br. *s*, NH_2); 6.64 (*m*, 1 arom. H); 7.40 (*m*, 5 arom. H). MS: 189 (M^+), 174, 115. Anal. calc. for $C_{11}H_{11}SN$ (189.29): C 69.8, H 5.9, N 7.4; found: C 70.0, H 5.9, N, 7.1.

8-(Methylthio)-1-naphthaleneamine (0.59 g, 3.12 mmol) was treated with 6M HCl (6 ml), cooled to –5°, and diazotised with a cold aq. soln. of $NaNO_2$ (230 mg, 3.33 mmol). The resulting brown mixture was quickly filtered, cooled again to –5°, and treated with a sat. aq. soln. of $NaBF_4$ (470 mg, 4.28 mmol) to give a brown precipitate. This product was collected by filtration, washed with cold MeOH followed by cold Et_2O, and then recrystallised from $MeCN/Et_2O$ to yield **2**·BF_4 (461 mg, 55%). M.p. 86–88° (dec.). IR (nujol): 2260. ^{1}H-NMR ((D_6)DMSO): 2.67 (*s*, Me); 8.12 (*m*, 4 arom. H); 8.98 (*d*, *J* = 9, H–C(4)); 9.36 (*d*, *J* = 9, H–C(2)). Anal. calc. for $C_{11}H_9BF_4N_2S$ (288.09): C 45.9, H 3.2, N 9.7; found: C 46.3, H 3.0, N 9.2.

8-(Dimethylamino)-1-naphthalenediazonium Tetrafluoroborate (**3**·BF_4). 8-(Dimethylamino)-1-nitronaphthalene, prepared by the procedures described in [37] [38], was reduced with a mixture of Et_3N and HCO_2H in the presence of 5% Pd-C to give *N,N*-dimethyl-1,8-naphthalenediamine which was purified by *Kugelrohr* distillation. B.p. 100°/0.05 Torr. This substance (186 mg, 1 mmol) was diazotised as described for **2**·BF_4. The product was recrystallised from $MeCN/Et_2O$ to yield **3**·BF_4 (201 mg, 70%). M.p. 90° (dec.).

8-Nitro-1-naphthalenediazonium Tetrafluoroborate (**4**·BF_4). 8-Nitro-1-naphthaleneamine (500 mg) [37] was diazotised as described for **2**·BF_4. The product was recrystallised from $MeCN/Et_2O$ to yield **4**·BF_4. Pale-pink crystals (275 mg, 36%). M.p. 115–118° (dec.; darkens at 80°). IR (nujol): 2225. ^{1}H-NMR ((D_6)DMSO): 2.80 (*s*, Me_2N); 7.90–8.28 (4 arom. H); 8.90 (*d*, *J* = 9, H–C(4)); 9.28 (*d*, *J* = 8, H–C(2)).

Determination of X-Ray Crystal Structures. Crystals of the BF_4 salts of **1**–**4** suitable for X-ray analysis were grown by cooling sat. solns. of the materials in $MeCN/Et_2O$ mixtures from r.t. to –10°. Although normal epoxy-resins did not completely secure a crystal of any of these materials to a glass fibre at r.t., the crystals became firmly attached at the lower temp. of the measurements. Diffraction intensities were measured on an *Enraf-Nonius CAD4* diffractometer equipped with a graphite monochromator (MoK_α radiation, μ = 0.71069 Å) and a cooling device. Crystal data for all four compounds are given in *Table 4*. The structures were solved by direct methods with MULTAN 80 [39] and refined by full-matrix least-squares analyses using the SHELX76 [40] and XRAY [41] program suites, including anisotropic displacement parameters for the non-H-atoms. An extinction correction was included in the refinement for **1**·BF_4 and **4**·BF_4. An exponential weighting scheme [42] was used in the final stages of the refinement of **1**·BF_4, **2**·BF_4, and **4**·BF_4. The crystal of **3**·BF_4 was disordered. An averaged structure was refined by applying geometric constraints (see *Table 4*), and unit weights were retained to the end of the refinement. Fractional atomic coordinates and anisotropic displacement parameters are given in the *Supplementary Material*.

Table 4. *Crystal Data for* $1 \cdot BF_4$–$4 \cdot BF_4$

	$1 \cdot BF_3$	$2 \cdot BF_4$	$3 \cdot BF_3$	$4 \cdot BF_4$
a [Å]	7.349(6)	7.260(2)	16.303(6)	10.821(2)
b [Å]	13.499(9)	14.625(4)	12.213(3)	9.548(2)
c [Å]	21.340(2)	11.846(3)	6.517(1)	11.151(2)
α [°]	90	90	90	90
β [°]	90	93.64(2)	90	109.22(2)
γ [°]	90	90	90	90
V [Å^3]	2103.6	1255.2	1297.6	1087.9
ρ_{calc} [g cm^{-3}]	1.64	1.52	1.46	1.75
T [K]	95	213	153	110
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group	$Pbca$	$P2_1/c$	$Pna2_1$	$P2_1/n$
Z	8	4	4	4
μ [cm^{-1}]	1.09	2.41	0.87	1.17
θ_{max} [°]	29	27	25	30
No. of measured reflections	3144	2735	2578	3145
No. of reflections with $I \geq 3\sigma(I)$	1926	1521	456	1970
$F(000)$	1040	584	584	576
Final R value	0.034	0.053	0.040	0.037
Final R_w value	0.035	0.056	–	0.045
Extinction parameter	1.04	–	–	0.14
H-Atom parameters	located, refined	located, refined	calculated, fixed	located, refined
Dunitz-Seiler weighting parameter	8	6	–	8

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