Incipient Nucleophilic Attack on a Nitrogen–Nitrogen Triple Bond: Crystal Structure of Quinoline-8-diazonium-1-oxide Tetrafluoroborate at 95 K

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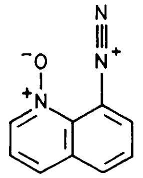
The interaction between the substituents in the title compound suggest that nucleophilic attack on the α-nitrogen atom of a diazonium group should occur preferentially at an angle of at least 104° to the triple bond.

Analysis of the ground-state structure of molecules containing neighbouring functional groups can provide information about preferred approach directions involved in possible chemical reactions between such groups.[1,2] We have now determined the crystal structure of the BF_4^- salt of cation (**1**) at 95 K to investigate the interaction between the nucleophilic oxygen atom and the N,N triple bond.

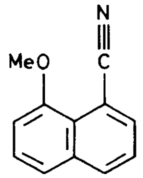
The orange salt was prepared by reaction of the corresponding primary amine[3] with isopentyl nitrite in ethanolic fluoroboric acid at −5 °C. Suitable crystals[†] were grown on cooling an acetonitrile–diethyl ether solution from 20 to −20 °C.

Crystal data for (**1**)·BF_4: $C_9H_6N_3O \cdot BF_4$, M = 258.9, orthorhombic, a = 7.349(6), b = 13.499(9), c = 21.205(14) Å at 95 K [a = 7.475(2), b = 13.506(3), c = 21.340(2) Å at 238 K], space group $Pbca$, Z = 8, D_c = 1.64 g cm^{-3}.

The structure was solved by direct methods and refined by full-matrix least-squares analysis[4,5] using the 1926 reflections measured with $I \geqslant 3\sigma(I)$ (Mo-K_α, $\lambda = 0.71069$ Å, $\theta \leqslant 29°$). All hydrogen atoms were located, and included in the refinement with isotropic vibration parameters (other atoms anisotropic). A modified weighting scheme[6] (r = 8 Å^2) and an extinction correction were applied in the final refinement cycles leading to R = 0.034 and R_w = 0.035.[‡] The structure of the cation is shown in Figure 1 and important features of the interaction are depicted in Figure 2. The BF_4^- group is ordered.



(**1**)



(**2**)

[†] *Spectroscopic data* for (**1**)·BF_4, m.p. 163 °C (decomp.): i.r. (Nujol mull) 2260 cm^{-1} (N≡N str.); ^{1}H n.m.r. δ [90 MHz, ($^2H_6$)dimethyl sulphoxide] 1-H 9.03(d), 3-H 7.96(q), 4-H 8.47(d), 5-H 9.05(d), 6-H 8.27(t), 7-H 9.55(d), $J_{2,3}$ 6, $J_{3,4}$ 9, $J_{5,6}$ 8, $J_{6,7}$ 8 Hz.

[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

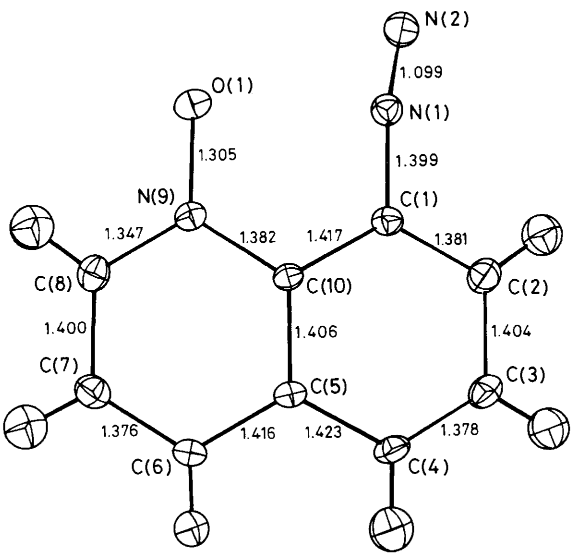


Figure 1. View of cation (**1**) (thermal vibration parameters drawn at the 50% probability level) with bond lengths indicated (Å) (e.s.d.s 0.002 Å, correction for rigid-body motion ≤ 0.002 Å, not included).

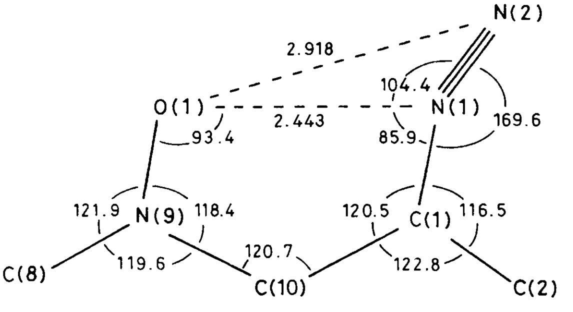


Figure 2. Non-bonded distances (Å) and angles (°) (e.s.d.s 0.1°) relevant to the O(1) · · · N(1)≡N(2) interaction. The other angles of the quinoline system lie in the range 118.0—121.2°. Deviations from the best plane of the quinoline system: O(1) +0.094, N(1) −0.192, N(2) −0.359, N(9) +0.032, C(1) −0.034 Å.

The oxygen atom lies 2.44 Å from the α-nitrogen atom of the diazonium group, well within the sum of the van der Waals radii. Nevertheless, the bonds to the substituents are not splayed apart in the plane of the ring [Figure 2; they are displaced to opposite sides of the best plane through the quinoline system, O(1) by 0.094 and N(1) by −0.192 Å, but this only increases the O(1) · · · N(1) separation by 0.017 Å]. Moreover, the diazonium group deviates by 10.4° from linearity in such a way that N(1) can be said to be displaced by 0.11 Å from the C(1) · · · N(2) direction *towards* O(1),§ strongly suggesting that the O(1) · · · N(1) interaction is attractive. We therefore feel justified in regarding it as an example of an incipient nucleophilic attack on a diazonium group.

If there were no interaction whatsoever between O(1) and N(1) we would expect to find two pairs of equal exocyclic angles at C(1) and N(9) of the quinoline system. What we actually find is an inward bending of the N(9)–O(1) bond accompanied by an outward bending of the C(1)–N(1) bond. Together with the outward bend at N(1) this produces an O(1)–N(1)–N(2) angle of 104.4°. The main factor controlling these distortions would seem to be the preferred geometry of the O · · · N≡N interaction since, unlike in (**2**), there is no steric hindrance to bond bendings in the opposite directions [outward bending of N(9)–O(1), inward of C(1)–N(1)], which would decrease the O(1) · · · N(1)–N(2) angle. The observed distortions thus support a preferred approach direction for the nucleophilic oxygen atom of 104° or more to the triple bond. [It seems highly unlikely that they are caused by packing effects, the closest contacts with fluorine being 3.23 Å to O(1), 2.79 Å to N(1), and 2.81 Å to N(2); *cf.* O(1) · · · N(1), 2.44 Å].

Our result fits well with other evidence on nucleophilic attack on triple bonds. Molecular orbital calculations[7] suggest an obtuse angle of approach for attack on the –C≡C– bond. The distortions in the nitrile (**2**)[2] suggest an angle of attack of at least 103° on a –C≡N bond. The nitrile group in (**2**) is less bent (173.2°) than the diazonium group in (**1**) (169.5°) in keeping with a somewhat stronger interaction in (**1**) between the formally charged groups. However, the exocyclic angular distortions in (**2**) are greater than in (**1**), because of the (O)Me · · · H repulsion which produces very similar distortions in anisoles.¶ On the other hand, as far as we are aware, there is no structural evidence for an acute angle of attack on the triple bond as once proposed by Baldwin.[8]

Attack on the α-nitrogen of a diazonium group to give an intermediate 1,1-diazene should perhaps not be discounted as a first step in a possible mechanism for nucleophilic substitution reactions involving this group.

We thank the Royal Society, London, for a European Science Exchange Fellowship to J. D. W.

Received, 7th March 1984; Com. 311

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§ In fact N(1) lies 0.012 Å from the plane defined by O(1), N(2), and C(1) but note that the positions of O(1), N(1), and N(2) may be slightly in error because their non-spherical electron distributions are not perfectly modelled by spherical atom form factors.

¶ The average values for the exocyclic angles in more than 30 anisoles with two *ortho* hydrogens and a C–C–O–Me torsion angle of <5° are 124.1(19) and 115.7(14)° (ref. 9).

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