The crystal structures of the BF₄⁻ salts of the 8-quinoindialzonium-1-oxide (1), 8-dimethylamino-naphthalene-1-diazonium (2) and 8-nitronaphthalene-1-diazonium (3) cations have been measured at low temperatures (85 - 150 K, R ≤ 0.04). All the structures show an interaction between the α-N of the diazonium group and a nucleophilic centre (α for 1 and β for 2). Distances between these interacting atoms lie in the range 2.44 - 2.54 Å, i.e. they are less than the sum of the appropriate van der Waals radii. The diazonium groups are bent (C-N = N angle of 171°) so that N₂ deviates from the C· · · N vector towards the nucleophilic centre.

In 1 and 2 the substituents are not splayed apart; instead the bond to the diazonium group bends outwards and the one to the nucleophilic centre bends inwards by a similar amount (1 by 2°, 2 by 3°). This helps to increase the C· · · N = N and N· · · N = N angles to 104 and 106° from near 90° in the undistorted molecule. Since in 1 there is no steric hindrance to distortion in the opposite direction the preferred direction of nucleophilic attack on the -N = N bond makes an angle of at least 104° to the bond axis.