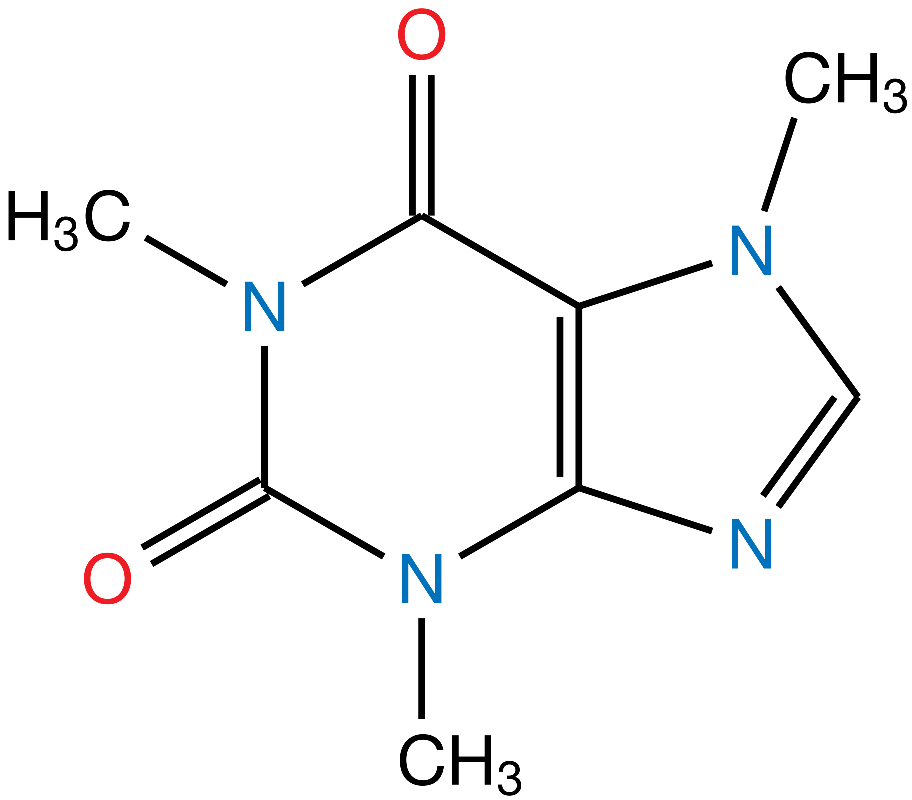
Organic Chemistry



$C_8H_{10}N_4O_2$

1,3,7-trimethylpurine-2,6-dione

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Caffeine

Chapters 8 to 12

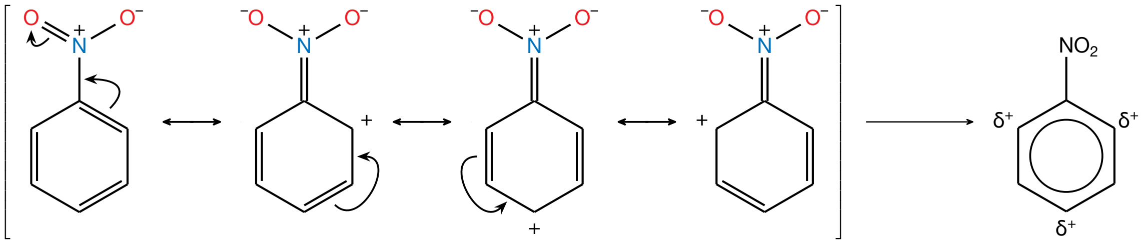
1 Arenes

1.0.1 Directing Mechanism

The exact mechanism behind the directing effects of substituents can be explored through the resonance structure of the substituted ring.

Electron-withdrawing Groups

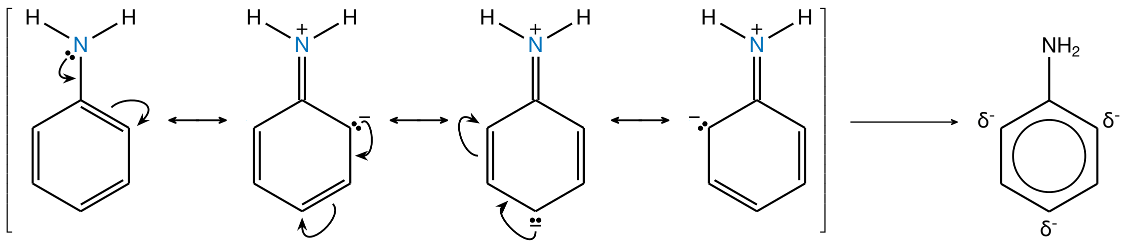
Taking nitrobenzene as an example, the attached NO_2 group is electron-withdrawing. As such, based on the resonance structure of the π-system below, there will be three points with a partial positive charge (δ^+). Since the substitution requires the attack of an *electrophile*, these positions are *less favourable*. Hence, the electrophile will tend to target the meta (or 3-directed) position, and the NO_2 group is said to be meta-directing, or 3-directing.



The δ^+ positions represent areas of low electron density.

Electron-donating Groups

On the other hand, for an electron-donating group such as NH_2, the reverse is true; there will be 3 areas of *high electron density* (actually the same 3 positions), which *attracts* electrophiles, and as such favours substituting further groups on the ortho/para positions, or 2,4 positions. Thus, NH_2 is said to be ortho/para-directing, or 2,4-directing.



The δ^- positions represent areas of low electron density.