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Crystal and Molecular Structures of Two *N*-Ammonio-amidates

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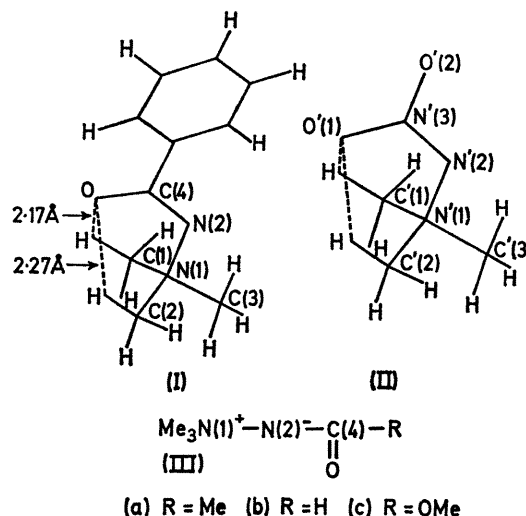
Summary Crystal structure analyses of the two nitrogen ylides (I) and (II) reveal that in both cases the quaternary nitrogen and delocalised anionic moieties adopt a synplanar relationship which results in possible interactions between oxygen and methyl hydrogen atoms.

For ylides of first-row elements, no formal bonding of the $d_{\pi}-p_{\pi}$ type between the onium group and the vicinal atom can occur.¹ As part of an examination of the extent to which this restriction affects the bonding and geometries of first-row ylides, we have determined the crystal structures of the *N*-trimethylammonioamidates (I)² and (II).³

Crystal data: (I), $C_{10}H_{14}N_3O$, monoclinic, $a = 11.62$, $b = 7.93$, $c = 11.45$ Å, $\beta = 113.8^\circ$, $Z = 4$, space group, $P2_1/c$; (II), $C_3H_9N_3O_2$, orthorhombic, $a = 12.25$, $b = 6.72$, $c = 7.10$ Å, $Z = 4$, space group, $Pnma$. A Hilger and Watts Y290 diffractometer was used to collect the 974 non-zero reflexions for (I) and 378 non-zero reflexions for (II). The structures were solved by symbolic addition procedures and in both cases all the hydrogen atoms were located by difference syntheses. Refinement of positional and anisotropic thermal parameters (isotropic for hydrogen atoms) was by block-diagonal least-squares calculations for (I) (final $R = 0.072$) and by full-matrix least-squares calculations for (II) (final $R = 0.078$). In the case of (II), the choice of space group $Pnma$ was vindicated by an attempted trial refinement with the non-restrictive symmetry of space group $Pna2_1$. The molecule (II) is thus restricted to possess mirror symmetry, the mirror plane containing the atoms O'(1), O'(2), N'(1), N'(2), N'(3), and C'(3).

The solid-state conformations of both (I) and (II) are very similar and are characterised by the synplanar relationships within the N(1)–N(2)–C(4)–O and N'(1)–N'(2)–N'(3)–O'(1) systems respectively. Synplanar relationships of onium and vicinal groups have been reported for certain other ylides.⁴ In both molecules the N(1) and N'(1) substituents and the methyl hydrogen atoms are fully staggered and the molecular conformations result in two

methyl hydrogen atoms of each molecule being close to the carbonyl and to one of the nitro-oxygen atoms respectively. The two relevant hydrogen atoms of (I) are separated from the carbonyl oxygen atom by 2.17(5) and 2.27(5) Å, while



in (II) the corresponding H...O distances are both 2.26(5) Å. The mean C–H...O angle for both molecules is 122°. For significant interaction to exist between hydrogen and oxygen atoms, it has been stated that the H...O separation may not be greater than 2.4 Å.⁵ A possible interpretation of the conformations and non-bonded separations of (I) and (II) is that in both molecules there exists a degree (at best very weak) of hydrogen-oxygen interaction. However, we have been unable to adduce any evidence for C–H...O hydrogen bonding in carbon disulphide solutions of (I) by variable temperature n.m.r. techniques, although intramolecular C–H...N

hydrogen bonding ($N \cdots H = 2.15 \text{ \AA}$, $C-H \cdots N$ angle = 128°) has been reported for the nitrogen terminus of a heteroenolate moiety ($-N^--C=O$) in an azomethine imine, a related ylide of different geometry.⁶

Comparison of relevant bond lengths in (I) and (II) reveals that the $N(1)-N(2)$ [$1.471(5) \text{ \AA}$] and $N'(1)-N'(2)$ [$1.470(8)$] bonds are identical within experimental error and are similar to single bonds in length. The $N(2)-C(4)$ [$1.313(6)$] and $N'(2)-N'(3)$ [$1.323(8)$] bonds are both slightly longer than expected for double bonds, thus possibly indicating that there is significant charge delocalisation on the carbonyl and nitro-oxygen atoms of (I) and (II),

respectively. Both the carbonyl bond of (I) [$1.243(5)$] and the nitro-bonds of (II) [mean length $1.259(6)$] are slightly longer than expected for similar bonds in environments where no charge delocalisation takes place, e.g. the N-O bonds of nitromethane possess lengths of 1.22 \AA .⁷

We have not found any evidence for conformational mobility around the $N(2)-C(4)$ bond in the *N*-ammonio-amidates (III a-c) by variable temperature n.m.r. spectroscopy.^{4,8} Temperature-invariant single singlet spectra were observed for all resonances over the temperature range -80 to $+110^\circ\text{C}$.†

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† For (IIIb) variations with temperature of the $-C(4)HO$ resonance were observed in accord with expectations based on temperature-dependent coupling between ^{14}N and a β hydrogen.

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