The Crystal and Molecular Structure of two Carbonyl-stabilised Ammonium Ylides

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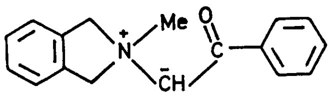
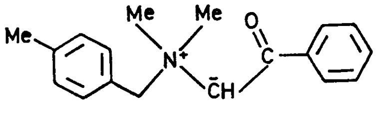
Summary The crystal structures of two carbonyl-stabilised, ammonium ylides are reported; bond lengths and angles indicate that the stabilisation results principally from electron delocalisation towards the carbonyl oxygen atom.

THE structures of a number of phosphonium ylides[1-4] (involving the grouping –P=C) are already known: recently, the preparation and characterisation of a novel series of carbonyl-stabilised, ammonium ylides has been reported.[5] The complete single-crystal, *X*-ray analysis of one such ylide (I) has been undertaken in order to confirm the formulation and to examine the nature of the means of stabilisation.


(I)


(II)

Compound (I) crystallises from water as anhydrous, colourless, elongated plates. *Crystal data:* $C_{17}ONH_{17}$, M 251·3, monoclinic, $a = 9{\cdot}52$, $b = 9{\cdot}79$, $c = 15{\cdot}04$ Å, $\beta = 107°8'$, $U = 1340$ Å^3, $D_m = 1{\cdot}30$, $Z = 4$, $D_c = 1{\cdot}25$, $F(000) = 536$, space group is $P2_1/c$.

Three-dimensional, *X*-ray data were collected photographically using, principally, equi-inclination Weissenberg geometry and Ni-filtered, Cu-$K\alpha$ radiation ($\bar{\lambda} = 1{\cdot}5418$ Å); the data, comprising 2144 independent reflections, were estimated visually and the usual corrections applied. The structure was solved by direct methods and has been refined by block-diagonal, least-squares methods to a current *R*-value of 0·092, anisotropic thermal motion being allowed for all non-hydrogen atoms. A difference Fourier synthesis has led to the assignment of positional parameters for all hydrogen atoms; contributions from these atoms have been included in the structure factor calculations but no refinement of parameters has been attempted.

The molecular geometry, including essential bond lengths and angles, is shown in the Figure (a); mean estimated standard deviations are 0·007 Å and 0·3°. It is clear from the slightly lengthened C–O and the short C(H)–C(O) bond lengths that the negative charge, formally located on the carbon atom, has delocalised towards the carbonyl oxygen atom, giving a geometry similar to those observed for the phosphonium ylides.[1,2] Supporting evidence for this delocalisation is provided by the coplanarity of the atoms of the N–C(H)–C(O)–C(Ph) grouping (r.m.s. deviation = 0·007 Å, plane A) and the trigonal planar co-ordination at the ylide carbon atom (shown by the determined position of the attached hydrogen atom). The angle between plane A and the mean plane of the terminal phenyl group is only 4° (corresponding twists in the phosphonium ylides[1,2] are 52 and 58°) but there is no evidence of further electron delocalisation towards the phenyl ring. The length of the N–C(H) bond is similar to the sum of covalent radii[6] and similar to that found in the structure of 5-(3-chlorobenzyldimethylammonium) tetrazolate[7] where the possibilities for electron delocalisation away from the carbon atom are much greater. Other bond lengths and angles are close to expected values.

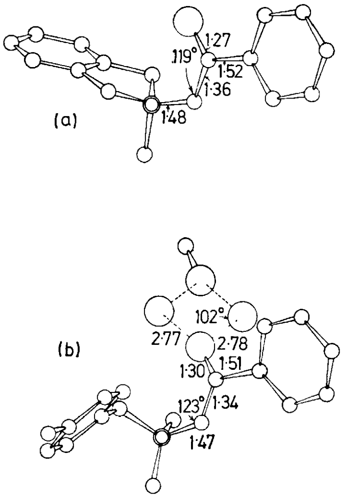


FIGURE. *The molecular geometries of* (a) *ylide* (I) *and* (b) *ylide* (II). *Carbon atoms are shown as small circles, oxygen atoms as large circles and nitrogen atoms as double circles.*

The structure determination of a second carbonyl-stabilised, ammonium ylide (II) is also reported. This molecule crystallises from water as the monohydrate in the form of pale yellow, elongated plates. *Crystal data:* $C_{18}O_2NH_{23}$, M 285·4, monoclinic, $a = 14{\cdot}58$, $b = 9{\cdot}26$, $c = 12{\cdot}29$ Å, $\beta = 94°40'$, $U = 1654$ Å^3, $D_m = 1{\cdot}13$, $Z = 4$, $D_c = 1{\cdot}15$, $F(000) = 616$, space group is $P2_1/c$.

Three-dimensional, *X*-ray data of only limited quality (1788 independent reflexions) were collected as for (I) and the structure solved in a similar manner; least-squares refinement (allowing individual isotropic thermal vibration parameters) has reduced *R* to 0·20. Preliminary results indicate that, within the common fragment, the bond lengths and angles are very similar to those of (I) but the angle between plane A and the plane of the terminal phenyl ring is 28°. In (II) the water molecule links centrosymmetrically related ylide molecules by the formation of hydrogen bonds to the carbonyl oxygen atoms [Figure (b)]. In view of the close similarity of the bond lengths and angles in the N–C(H)–C(O)–Ph regions of both molecules, it appears that proton transfer from the water to form a quaternary ammonium hydroxide has *not* occurred; thus, within the limits of the present analysis, (II) can also be formulated as a carbonyl-stabilised, ammonium ylide. A more detailed analysis of (II) is in progress.

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