The Crystal Structure of a Novel Heterocycle containing an Intramolecular Carbon–Nitrogen Hydrogen Bond

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A CRYSTAL structure investigation of the novel compound α-1-(p-bromophenyl)phenylmethylene-3-oxo-1,2-diazetidinium inner salt, (I), synthesized by Greenwald and Taylor,[1] has revealed several interesting features, including an intramolecular C–H · · · N hydrogen bond, and a CCN angle of only 81° within the four-membered ring. Only one other example, crystalline hydrogen cyanide,[2] is known in which carbon serves as a hydrogen-bond donor to an acceptor nitrogen.

The crystals are of approximately equidimensional habit. A specimen about $0.35 \times 0.25 \times 0.60$ mm. was cut and mounted about the long dimension (b-axis) for diffraction study. Weissenberg and precession photographs revealed monoclinic symmetry, with absences characteristic of space group $P2_1/c$. Preliminary unit-cell constants from film measurements were refined with the aid of a Picker four-circle diffractometer to final values of $a = 11.90 \pm 0.01$, $b = 7.38 \pm 0.01$, $c = 17.28 \pm 0.01$ Å, and $\beta = 119.44 \pm 0.02°$. Intensity data were collected on an automatic Picker four-circle diffractometer using Zr-filtered Mo-K_α radiation. A scintillation counter, with pulse-height discriminator set to accept 90% of the K_α pulse distribution, served as radiation detector. All peaks having $2\theta \leq 60°$ were scanned in 2θ using a scan range of $2.0°$ and a scan rate of $1°$/min. A 20 sec. stationary background count was made at either end of the scan range. Structure factors and their standard deviations were extracted in the usual way,[3] with application of appropriate Lorentz and polarization corrections No correction was made for absorption. The set of measured data consisted of 1517 observed and 321 "unobserved" reflections, the latter below observational threshold.

The structure was solved by the heavy-atom technique and refined by least-squares to a current R of 5·6%. All hydrogen atoms were located in a different map. The bond distances given in the Figure indicate that the valence structure (I) is a fairly accurate representation of the bonding. Reference to a compilation[4] of many bond lengths reveals that C(18)–O(19) and C(8)–H(15) qualify as essentially normal double bonds. However, both N(15)–N(17) and especially N(17)–C(18) are shorter than would be expected for single bonds and this might be taken as an indication of

resonance. Consistent with some aromatic character in the methylene-oxo-azetidinium moiety is the fact that it is completely planar within experimental error ($\sigma_C \approx 0.005$ Å). Nevertheless this compound is quite unusual and probably involves a fair degree of charge separation in its ground state. One must therefore be careful in drawing comparisons with "normal" double- and single-bond lengths.
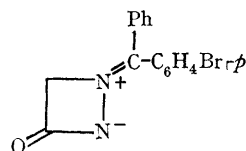
A feature of considerable interest in this structure is the internal C–H · · · N hydrogen bond formed between C(6) and N(17). Phenyl ring A is within 6° of the methylene-oxo-azetidinium plane, whereas phenyl group B is inclined at 89·5° to this plane. Although gain in delocalization energy as well as hydrogen-bond formation favour a planar
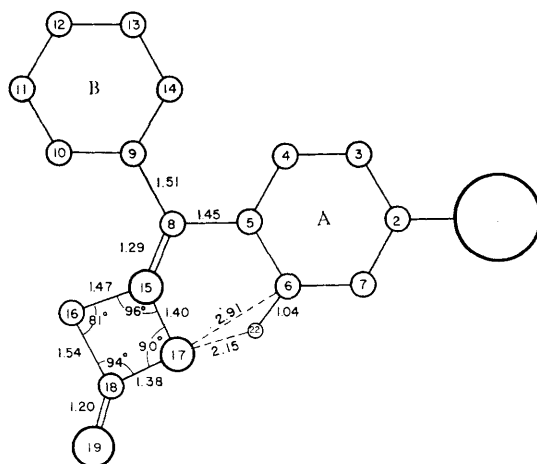
structure, the N(17) · · · H(22) contact of 2·15 Å is too short to be referred to other than as a hydrogen bond. The sum of van der Waals radii[5] (2·7 Å) so far exceeds the actual contact, that it is most unlikely that gain in resonance energy alone would

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produce a planar structure. Further, the H $\cdots$ N contact is quite similar to that (2·2 Å) in the only other structure known to contain a C-H $\cdots$ N bond, HCN.[2] The C $\cdots$ N distance of 2·91 $\pm$ 0·02 Å in the present structure is considerably shorter than that in HCN because the C-H $\cdots$ N angle is 128° in the present case rather than 180°.

The C-H $\cdots$ N bond is favoured by the high formal negative charge on N(17). Molecular orbital calculations indicate a comparatively large negative charge on this atom. The relative weakness of this hydrogen bond is emphasized by the fact that in the n.m.r. spectrum of the corresponding unbrominated material,[2] two rather than one of the ten aromatic protons are shifted downfield, (δ 7·92 cf. 7·41 for the remaining eight). Therefore, in solution, this "bond" is little more

than a shallow minimum in the rotational potential of the phenyl ring.

A second unusual feature of this structure is the small angle of 81·3° at C(16), especially as so much of the angle strain appears to be localized at this carbon. This can be rationalized since one would expect the angles at approximately sp^2 N(15) and C(18) to be larger than those at C(16) or N(17). In fact the overall geometry of diketen,[5] isoelectronic with the methylene-oxo-azetidinium moiety, is strikingly similar. In particular the angle corresponding with that at C(16) is 83°.

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