Crystal and Molecular Structure of the Hydrogen-Bonded Adduct of Pyridine N-Oxide with Trichloroacetic Acid

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Summary The molecules of pyridine N-oxide and trichloroacetic acid are connected by an extremely short hydrogen bond (2·41 Å) in the pyridine N-oxide–trichloroacetic acid adduct.

THE i r. spectrum of the adduct of pyridine N-oxide (PyO) with trichloroacetic acid (TCA) has the same characteristic features of the hydrogen bond as some acid salts of carboxylic acids.[1] These spectra do not contain any bands in the region above 1700 cm^{-1} that can be attributed to O–H stretching, but a strong absorption around 1000 cm^{-1} which possibly represents this vibration. Such spectra in general have been labelled type (ii)[2] or, for acid salts, type A[3] and were successfully used in the search for possibly symmetrical O $\cdots$ H $\cdots$ O bonds. In the PyO–TCA adduct the necessary condition for symmetrical hydrogen bonding (a bond between an acid and its conjugate base) is not fulfilled and thus it was puzzling to find spectra of type (ii) for this and some similar adducts.[1] An explanation[4] was the formation of double ion pairs (PyO $\cdots$ H $\cdots$ PyO)$^+$(TCA $\cdots$ H $\cdots$ TCA)$^-$. The arguments in favour of this were as previously reported[2] for the PyO–TCA structure. An X-ray crystallographic structure determination was undertaken in order to decide between the two possibilities.

Crystals of the PyO–TCA adduct were grown from a chloroform solution of both components. $C_5H_5NO,C_2HCl_3O_2$, $M = 258\cdot5$, monoclinic, $a = 11\cdot745(2)$, $b = 9\cdot120(3)$, $c = 10\cdot609(4)$ Å, $\beta = 108\cdot85(03)°$, $U = 1075$ Å^3, $D_m = 1\cdot56$, $Z = 4$, $D_c = 1\cdot596$, space group $P2_1/c$ (No. 14). Intensities were recorded photographically with a Weissenberg camera and Cu-K_α radiation and visually estimated.

The structure was solved by standard Patterson and Fourier methods and is shown with pertinent bond distances in the Figure. The distances may be slightly different after the least-squares refinement, but the essential point of the bonding of one molecule of PyO to one of TCA is certain as is the extreme shortness of the O $\cdots$ O contact. The refinement based on 1210 reflections which has now reached $R = 9\cdot3\%$ gives 2·411(8) Å for this distance.

One possible conclusion is that the part of the potential function of the proton which is effective for the lowest vibrational levels is not affected by the asymmetry of bonding in the adduct. An alternative is that the potential in the acid salts is also asymmetric. From structural considerations one may expect here either a symmetrical single minimum or a symmetrical double minimum potential, but no asymmetric one.
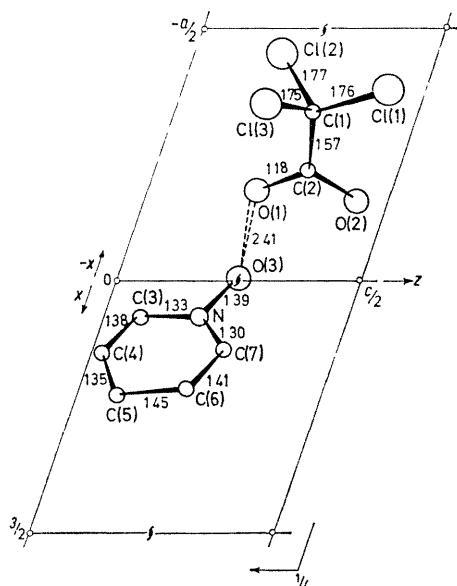

FIGURE. *Pyridine N-oxide–trichloroacetic acid adduct*

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[2] D. Hadži, *Pure Appl. Chem.*, 1965, **11**, 435.
[3] M. Currie and J. C. Speakman, *J. Chem. Soc.* (*A*), 1970, 1923.
[4] M. Szafran, *Bull. Acad. polon. Sci., Ser. Sci. chim.*, 1964, **12**, 383.