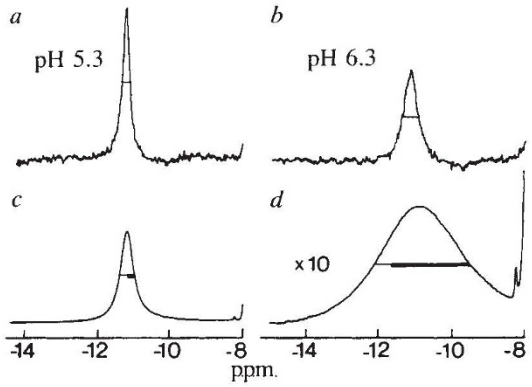

Fig. 4 Imino proton transfer from uridine (represented here by UH) to water, measured by line-broadening of the imino proton spectrum. *a*, *b*, The uridine concentration is 10 mM. Proton transfer is catalysed by H_2O at *p*H 5.3 and OH^- at *p*H 6.3. The concentration of U^- ion is too small to affect proton exchange. *c*, *d*, The uridine concentration is 1.16 M. The concentration-dependent increments of the linewidth are 50 and 558 Hz. Their ratio is close to the ratio (1:10) of the pH-dependent U^- concentrations, showing that the incremental width, represented by a heavy line, is due to indirect proton transfer to water through a UH···OHH···U^- complex. The spectra are scaled according to the uridine concentration. The temperature was 25 °C.

Lacking an experimental model of indirect back-transfer for the AH^+/T^- couple, we illustrate the transfer to water by the homologous couple UH/U^- (Fig. 4).

For a large collision rate, the two bases should remain close to one another in the open state. Together with the requirement for indirect back-transfer, this suggests that an open-state structure in which hydrogen-bonded water bridges the N_1 of adenosine to the $-N_3H$ of thymidine should be considered. Preliminary evaluations indicate that such a structure could account for the observed AAC exchange times.

It was mentioned above that the ratio between the rates of exchange by the AAC mechanism and by ammonia catalysis will be constant only if the chemistry of exchange itself is not strongly temperature-dependent. This can be explored theoretically, by considering the temperature dependence of *pK* and of diffusion rates, or experimentally, by measuring exchange catalysis of mononucleosides at different temperatures, as will be reported in detail elsewhere. We point out here that the efficiency of ammonia as a catalyst of nucleosides is nearly independent of temperature, due to the compensating variations with temperature of the difference between its pK and that of nucleosides and of its diffusion constant. As for the *pK* difference between adenosine and thymidine, its variation should change the rate of catalysis by a factor of ~1.2 over 10 deg C, and the effect is even smaller for a G·C pair. Such variations are too small to affect the interpretation of the data of Fig. 2.

The identification of the other base of the pair as the intrinsic catalyst is, in our opinion, plausible but not yet established. However this does not alter the strong evidence presented above that ammonia-catalysed exchange and AAC exchange proceed from the same open state.

In conclusion, a single kinetic process is reponsible for all features of imino proton exchange in the deoxyribonucleic acids studied here. Exchange occurs from the open state. It is catalysed both by added catalysts such as ammonia and by an intrinsic catalyst, probably the other base of the pair. In the latter case, proton transfer to water would occur during proton back-transfer through a bridging water molecule. The long catalyst-independent exchange time observed at low catalyst concentrations is unrelated to base-pair lifetime. We propose the present model for the interpretation of imino proton exchange in A, B and Z duplexes and in transfer RNA.

This process may be the principal mode of base-pair disruption, or even the only one, at temperatures well below melting. Its properties are presently under investigation and some characteristic results have been presented earlier[1,2]. At 25 °C, lifetimes are typically in the region of 10 ms. Dissociation constants are in the region of 10^{-5} for oligo-deoxyribonucleic acids. Internal base pairs open one at a time and their lifetime shows some sensitivity to the nature of the base pair and to the DNA sequence.

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Corrigendum

The optical polarization of the Sun, measured at a sensitivity of parts in ten million

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IN this paper I. S. Beardsley was omitted from the published list of authors.

Erratum

Quasicrystal morphologies

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