2-Aminopurine: A Probe of Structural Dynamics and Charge Transfer in DNA and DNA:RNA Hybrids

Melanie A. O'Neill and Jacqueline K. Barton*

Contribution from the Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

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Abstract:

Spectroscopic techniques are employed to probe relationships between structural dynamics and charge transfer (CT) efficiency in DNA duplexes and DNA:RNA hybrids containing photoexcited 2-aminopurine (Ap*). To better understand the variety of interactions and reactions, including CT, between Ap* and DNA, the fluorescence behavior of Ap* is investigated in a full series of redox-inactive as well as redox-active assemblies. Thus, Ap* is developed as a dual reporter of structural dynamics and base-base CT reactions in nucleic acid duplexes. CD, NMR, and thermal denaturation profiles are consistent with the family of DNA duplexes adopting a distinct conformation versus the DNA:RNA hybrids. Fluorescence measurements establish that the d(A)-r(U) tract of the DNA:RNA hybrid exhibits enhanced structural flexibility relative to that of the d(A)-d(T) tract of the DNA duplexes. The yield of CT from either G or 7-deazaguanine (Z) to Ap* in the assemblies was determined by comparing Ap* emission in redox-active G- or Z-containing duplexes to otherwise identical duplexes in which the G or Z is replaced by inosine (I), the redox-inactive nucleoside analogue. Investigations of CT not only demonstrate efficient intrastrand base-base CT in the DNA:RNA hybrids but also reveal a distance dependence of CT yield that is more shallow through the d(A)-r(U) bridge of the A-form DNA:RNA hybrids than through the d(A)-d(T) bridge of the B-form DNA duplexes. The shallow distance dependence of intrastrand CT in DNA:RNA hybrids correlates with the increased conformational flexibility of bases within the hybrid duplexes. Measurements of interstrand base-base CT provide another means to distinguish between the A- and B-form helices. Significantly, in the A-form DNA:RNA hybrids, a similar distance dependence is obtained for inter- and intrastrand reactions, while, in B-DNA, a more shallow distance dependence is evident with interstrand CT reactions. These observations are consistent with evaluations of intra- and interstrand base overlap in A- versus B-form duplexes. Overall, these data underscore the sensitivity of CT chemistry to nucleic acid structure and structural dynamics.

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