86-2; propiophenone, 93-55-0; *trans*-stilbene, 103-30-0; 4-methylacetophenone, 122-00-9; 4-methoxyacetophenone, 100-06-1; cyanobenzene, 100-47-0; methyl benzoate, 93-58-3; ethyl benzoate, 93-89-0; 3,5-dichloropyridine, 2457-47-8; 3-cyanopyridine, 100-70-9; 4-cyanopyridine, 100-48-1; 3-bromopyridine, 626-55-1; 3-acetylpyridine, 350-03-8; 4-acetylpyridine, 1122-54-9; pyridine, 110-86-1; 2-aminopyridine, 504-29-0; 2,3-dichloro-5,6-dicyano-*p*-benzene, 84-58-2; 2,3-dicyano-*p*-benzoquinone, 4622-04-2; *p*-chloranil, 118-75-2; *p*-bromanil, 488-48-2; 2,6-dichloro-*p*-benzoquinone, 697-91-6; 2,5-dichloro-*p*-benzoquinone, 615-93-0; chloro-*p*-benzoquinone, 695-99-8; *p*-benzoquinone, 106-51-4; methyl-*p*-benzoquinone, 553-97-9; 2,6-dimethyl-*p*-benzoquinone, 527-61-7; trimethyl-*p*-benzoquinone, 935-92-2; magnesium, 22537-22-0.

Isotopic Multiplets in the Carbon-13 NMR Spectra of Aniline Derivatives and Nucleosides with Partially Deuterated Amino Groups: Effects of Intra- and Intermolecular Hydrogen Bonding

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Abstract: In aniline derivatives, the carbon-13 resonances of atoms bearing partially deuterated amino groups, as well as the resonances of vicinal carbon atoms, appear as multiplets. This phenomenon, which is due to upfield deuterium isotope effects on carbon-13 chemical shifts, is observed under conditions of slow hydrogen exchange (e.g., in Me_2SO solutions). The effects are larger for groups engaged in intramolecular hydrogen bonds. Empirical expressions are presented that relate isotope effects with amino proton chemical shifts and hydrogen bond energies. Isotopic multiplets are also observed in the carbon-13 NMR spectra of partially deuterated nucleosides. The multiplet structure is altered upon formation of base pairs. These results are interpreted in terms of hydrogen exchange reactions involving uridine (or thymidine) hydrogen-bonded dimers or changes in hydrogen bond energies upon formation of guanosine–cytidine complexes. Estimates are given for the energies of individual hydrogen bonds in Watson–Crick base pairs.

The conformation, properties, and function of organic molecules in aqueous solution, including biological and synthetic polymers, depend to a large extent on the phenomenon of hydrogen bonding. Because of its fundamental importance, this phenomenon has been the subject of extensive studies by all of the available spectroscopic techniques.[1] Recently a correlation was observed between deuterium isotope effects on carbon-13 chemical shifts and hydrogen bond energies for phenolic and enolic hydroxyl groups engaged in intramolecular hydrogen bonds.[2] This paper presents results on isotopic multiplets in carbon-13 NMR spectra and deuterium isotope effects on carbon-13 chemical shifts for aniline derivatives and nucleosides. In selecting compounds for investigation, particular attention was paid to the possible presence or absence of hydrogen bonding phenomena.

Carbon atoms in the vicinity of partially deuterated functional groups containing exchangeable hydrogens exhibit multiplet structure in the proton-decoupled carbon-13 NMR spectrum. These multiplets result from small upfield deuterium isotope effects on the carbon-13 chemical shifts and are observable under conditions of slow (relative to the magnitude of the isotope effect) chemical exchange between the protio and deuterio forms.[3] Hydrogen ion exchange for amino groups attached to aliphatic carbons is usually fast but slows down considerably upon protonation or coordination to a metal ion. Indeed, isotopic multiplets have been observed in the carbon-13 NMR spectra of ammonium ion derivatives[4] and cobalt(III) complexes.[5] The basicities of aniline derivatives as well as of other conjugated amines are much lower than those of aliphatic amines. Resolved proton resonances of amino and imino groups of such materials in nonhydroxylic solvents can be observed and the results of spin coupling to protons on α carbons can be discerned.[6] Therefore, the observation of isotopic multiplets in their carbon-13 NMR spectra could be anticipated.

Intramolecular hydrogen bonding in aniline derivatives with carbonyl or nitro groups in the ortho position is a well-known phenomenon established on the basis of infrared spectral evidence.[7] The amino proton shifts also indicate the presence of such interactions.[8] Watson–Crick base pairing of nucleosides through intermolecular hydrogen bonds has been the subject of numerous investigations by NMR spectroscopy. Thus, e.g., Katz and Penman showed that formation of stable complexes between guanosine and cytidine in Me_2SO solutions leads to substantial downfield shifts of the amino and imino protons.[9] Subsequently Newmark and Cantor obtained thermodynamic data in the same system from the concentration and temperature dependencies of the proton shifts.[10] More recently Petersen and Led conducted a similar investigation by carbon-13 NMR spectroscopy.[11] Substantial downfield shifts upon base pairing were observed for all of the base carbons, except for carbon-5 of guanosine, which shifted upfield. However, in Me_2SO as the solvent no interaction between adenosine and uridine or thymidine could be detected either by proton[9] or carbon-13 NMR.[12] In order to study the

(1) Vinogradov, S. N.; Linnell, R. H. *Hydrogen Bonding*; Van Nostrand-Reinhold: New York, 1971.
(2) Reuben, J. *J. Am. Chem. Soc.* **1986**, *108*, 1735-1738.
(3) For a review see: Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 105-234.
(4) Reuben, J. *J. Am. Chem. Soc.* **1985**, *107*, 1433-1435.
(5) Yashiro, M.; Yano, S.; Yoshikawa, S. *J. Am. Chem. Soc.* **1986**, *108*, 1096-1097.
(6) Pouchert, C. J. *The Aldrich Library of NMR Spectra*; Aldrich: Milwaukee, 1983.
(7) Dyall, L. K. *Spectrochim. Acta, Part A* **1969**, *25*, 1727-1741 and references therein.
(8) Yonemoto, T.; Reynolds, W. F.; Hutton, H. M.; Schaefer, T. *Can. J. Chem.* **1965**, *43*, 2668-2677.
(9) Katz, L.; Penman, S. *J. Mol. Biol.* **1966**, *15*, 220-231.
(10) Newmark, R. A.; Cantor, C. R. *J. Am. Chem. Soc.* **1968**, *90*, 5010-5017.
(11) Petersen, S. B.; Led, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 5308-5313.

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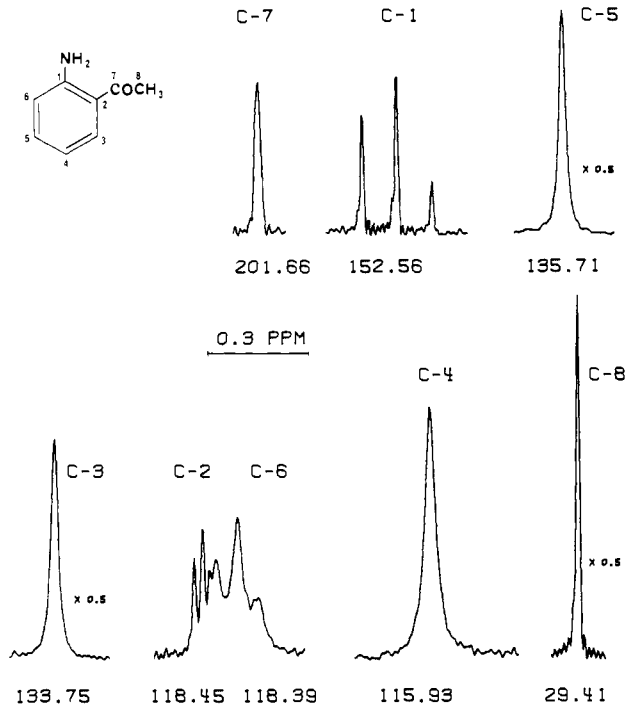


Figure 1. The carbon-13 resonances of partially deuterated *o*-aminoacetophenone (**5**)[17] showing isotopic multiplets. The chemical shifts (in ppm) for the protio form are listed under each spectral band.

corresponding base pairs, derivatives of the bases, e.g., 9-ethyladenine and 1-cyclohexyluracil, were employed and chloroform was used as the solvent.[9,13]

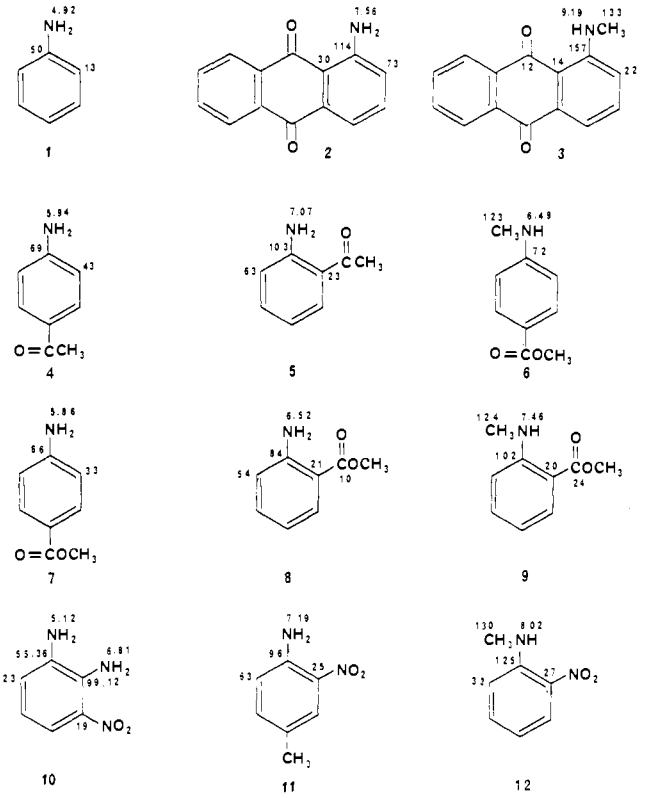
Experimental Section

The experimental details are similar to those previously reported.[2] All of the materials were obtained from commercial sources. The solvent was Me_2SO-d_6, except for 1-(methylamino)anthraquinone (**3**) which was dissolved in $CDCl_3$. The concentrations were ca. 0.2 M. Partial deuteration was achieved by the addition of a calculated amount of CH_3OD such that the H/D ratio would be (slightly) greater than unity. The latter detail is important for determining the sign of the isotope effect. Carbon-13 NMR spectra were recorded at ambient temperature (24 ± 1 °C) with a Nicolet 360 WB spectrometer operating at 90.56 MHz in the pulsed Fourier transform mode with low-power broad-band proton decoupling. Chemical shift assignments for the aniline derivatives were made by using the well-established substituent effects on carbon-13 chemical shifts.[14] The attached proton test[15] or coupling constants with protons[14] were used in resolving a few ambiguities. Assignments for the nucleosides were taken from literature references.[11,12,16] Proton chemical shifts of the amino groups in the same solutions were measured at 90 MHz with a Varian EM-390 spectrometer. The characteristic broad shape of these resonances facilitates their assignment.

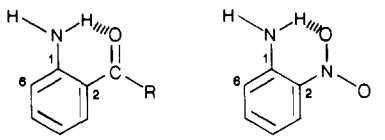
Results and Discussion

Aniline Derivatives.[17] A summary of deuterium isotope effects on carbon-13 chemical shifts and amino proton shifts is given in Chart I. An example of isotopic multiplets is presented in Figure 1, where the carbon-13 resonances of **8** with partially deuterated amino group are shown. A number of features are noteworthy. (1) Only carbon 1 and the ortho carbons exhibit multiplet

Chart I. Deuterium Isotope Effects on Carbon-13 Chemical Shifts (in ppb/deuteron) and Amino Proton Chemical Shifts (in ppm) for Aniline Derivatives



structure. (2) The multiplets are triplets (corresponding to the NH_2, NHD, and ND_2 species), indicating that the amino hydrogens are equivalent (i.e., two equivalent NHD species) on a time scale defined by the magnitude of the isotope effect. (3) The isotope effect on carbon 1 ($^2\Delta$) is larger than that on the ortho carbons ($^3\Delta$), i.e., $^2\Delta > {}^3\Delta$. (4) The isotope effect on carbon 6,



which is protonated and anti to the intramolecular hydrogen bond, is larger than that on carbon 2, which is substituted and syn to the hydrogen bond. A similar relation has been observed for $^3\Delta$ from hydrogen-bonded OH groups in phenol derivatives.[2]

Previous work on phenol derivatives with intramolecular hydrogen bonds has shown that the two-bond isotope effect, $^2\Delta$, correlates with the hydrogen bond energy.[2] The latter was calculated from the hydroxyl proton shift by using the empirical relation of Schaefer.[18] Although the precise dependence of the amino proton shift on the hydrogen bond energy has not been determined, one may assume that the two quantities are related.[8] Therefore, correlations between isotope effects on carbon-13 chemical shifts and amino proton shifts were sought. The results are plotted in Figure 2. The correlations are linear to a good approximation. The following relationships were obtained by linear regression analysis (correlation coefficients in parentheses):

$$^2\Delta = -68.4 + 23.6\delta_{NH_2} \quad (r = 0.987) \quad (1)$$

$$^3\Delta_{CH,anti} = -89.9 + 21.6\delta_{NH_2} \quad (r = 0.989) \quad (2)$$

$$^3\Delta_{CR,syn} = -23.1 + 6.67\delta_{NH_2} \quad (r = 0.942) \quad (3)$$

where the isotope effects are in ppb and the amino proton shifts in ppm. The result of 36 ppb for $^3\Delta$ at C-1 of 3-nitro-1,2-

(12) Abbott, D. W.; Woods, C. *Inorg. Chem.* **1983**, *22*, 2918–2923.
(13) Iwahashi, H.; Kyogoku, Y. *J. Am. Chem. Soc.* **1977**, *99*, 7761–7765.
(14) Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Heyden: London, 1980.
(15) Patt, S. L.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535–539. Le Cocq, C.; Lallemand, J. Y. *J. Chem. Soc., Chem. Commun.* **1981**, 150–152.
(16) Jones, A. J.; Grant, D. M.; Winkley, M. W.; Robins, K. K. *J. Am. Chem. Soc.* **1970**, *92*, 4079–4087. Mantsch, H. H.; Smith, I. C. P. *Biochem. Biophys. Res. Commun.* **1972**, *46*, 808–815. Chandrasegaran, S.; Kan, L. S.; Sillerud, L. O.; Skoglund, C.; Bothner-By, A. A. *Nucleic Acids Res.* **1985**, *13*, 2097–2110.
(17) The aniline numbering scheme is used throughout this paper; i.e., the atom bearing the amino group is always designated as carbon-1.
(18) Schaefer, T. *J. Phys. Chem.* **1975**, *79*, 1888–1890.

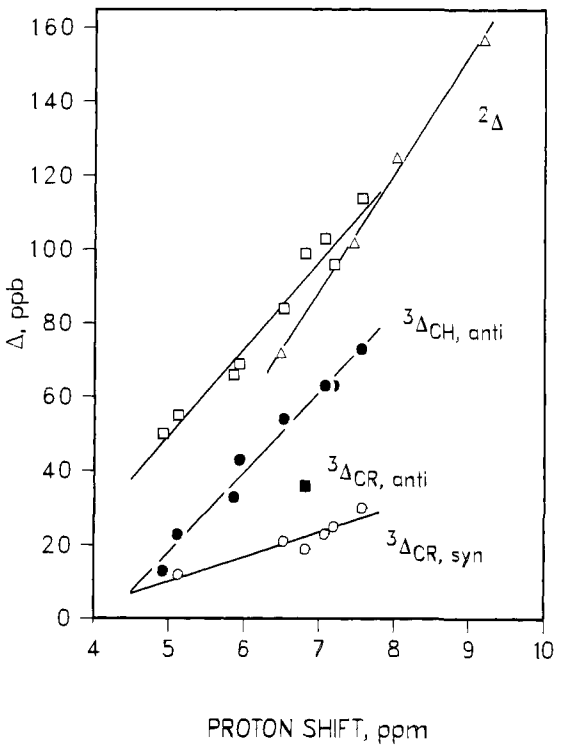


Figure 2. A plot of deuterium isotope effects on carbon-13 chemical shifts of aniline derivatives against the amino proton chemical shifts. The triangles are for $^2\Delta$ of the *N*-methyl derivatives (**3**, **6**, **9**, and **12**).

phenylenediamine (**10**) (see Figure 2) indicates that $^3\Delta$ depends both on the state of protonation of the affected carbon atom and its disposition relative to the hydrogen bond. For the *N*-methyl derivatives only the values of $^2\Delta$ exhibit similar trends:

$$^2\Delta = -133.9 + 31.8\delta_{NH} \qquad (r = 0.998) \qquad (4)$$

These correlations suggest that the isotope effects on carbon-13 chemical shifts are strongly influenced by hydrogen-bonding interactions. In the absence of suitable ortho substituents, these must be intermolecular interactions of the solute–solvent and the solute–solute types. An obvious indication for the importance of such interactions is the large chemical shift difference for the amino protons of aniline (**1**) between $CDCl_3$ (δ 3.33 ppm)[6] and Me_2SO-d_6 (δ 4.92 ppm, Chart I) solutions. The above correlations can be useful in making spectral assignments. Thus, e.g., they were used in assigning the amino resonances of 3-nitro-1,2-phenylenediamine (**10**) and in tracing the origins of the two isotope effects on carbon 1.

The magnitude of the two-bond isotope effect, $^2\Delta$, due to NH_2 and CH_3NH groups in aniline derivatives is relatively small and spans the narrow range of 50–157 ppb. On the other hand, the values for phenolic and enolic hydroxyls are much larger and span the much wider range of 227–1044 ppb.[2] The main reason for this disparity seems to be the large difference in the corresponding hydrogen bond energies: 7–12 kcal/mol for intramolecular hydrogen bonds of the OH···O type,[2] but only 3–6.5 kcal/mol for bonds of the NH···O type.[1] Assuming that $^2\Delta$ is governed largely by hydrogen bonding interactions, one may use the previously obtained[2] empirical relation between $^2\Delta$ and the hydrogen bond energy, *E*, in order to calculate values of *E*. These can be used in turn to obtain a relation between the proton chemical shift and the hydrogen bond energy. The results are

$$\Delta\delta_{NH_2} = 1.46 + E \qquad (5)$$

where $\Delta\delta_{NH_2}$ is the chemical shift of the amino protons in ppm relative to that of aniline in $CDCl_3$ (3.33 ppm)[6] and *E* is in kcal/mol. A similar relation,

$$\Delta\delta_{NH} = -1.06 + E \qquad (6)$$

was obtained for *N*-methyl derivatives, with $\Delta\delta_{NH}$ being referred to the proton shift of the NH of *N*-methylaniline in $CDCl_3$ (3.50 ppm).[6]

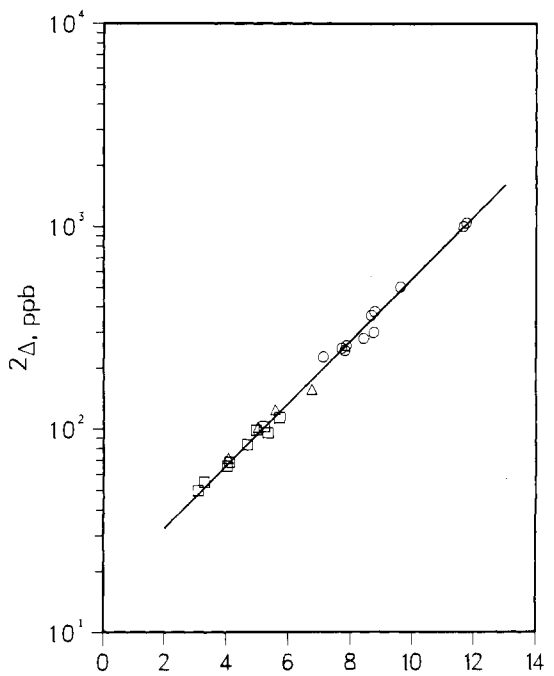


Figure 3. A plot of the two-bond isotope effect, $^2\Delta$, against the hydrogen bond energy, *E*, as obtained from hydroxyl or amino proton chemical shifts: ○, intramolecularly hydrogen-bonded phenolic and enolic hydroxyls (data from ref 2); □, aniline derivatives; △, *N*-methyl derivatives.

A plot of $^2\Delta$ (on a logarithmic scale) against the values of *E* obtained with eq 5 and 6 is shown in Figure 3. Also plotted there are the data on the phenolic and enolic hydroxyls.[2] A linear regression analysis, which included all of the data given in Figure 3, yielded the relation

$$\ln(^2\Delta) = 2.817 + 0.35E \qquad (r = 0.997) \qquad (7)$$

The relations of eq 5 and 6 provide a means of obtaining hydrogen bond energies on a *relative* scale. The use of isotope effects (eq 7) for this purpose, rather than proton shifts (eq 5 and 6), may have a definite advantage in cases where the proton shifts contain substantial contributions from diamagnetic effects (e.g., ring currents) of the environment. Such would be the case of base pairing between nucleosides (or other nucleic acid components), which is discussed in the next section.

Nucleosides. Five nucleosides were investigated in this work: adenosine (A), guanosine (G), uridine (U), thymidine (T), and cytidine (C). A summary of deuterium isotope effects on carbon-13 chemical shifts is given in Chart II. Multiplet (doublet) structures due to partial deuteration of the imino groups of uridine and thymidine were observed only when adenosine was also present in the same solution (vide infra). The isotope effects on the ribose carbons are in general similar to those reported for β-D-ribofuranose.[19] The only discrepancies, the reasons for which are unknown, are the two equal effects on C-4′ of uridine and cytidine. The effects due to the amino and imino groups are within the ranges observed in aniline derivatives (see, e.g., Figure 2). A three-bond effect ($^3\Delta$) from an imino group was resolved only in thymidine (when complexed with adenosine). These observations are in accord with the results for *N*-methyl derivatives (see Chart I) for which $^3\Delta$ is either very small or unresolved.

Upon partial deuteration of the amino group of adenosine, the resonances of carbon 5 and 6 split into triplets as shown in Figure 4. Apart from some line broadening, very little change is observed

(19) Reuben, J. *J. Am. Chem. Soc.* **1984**, *106*, 6180–6186.

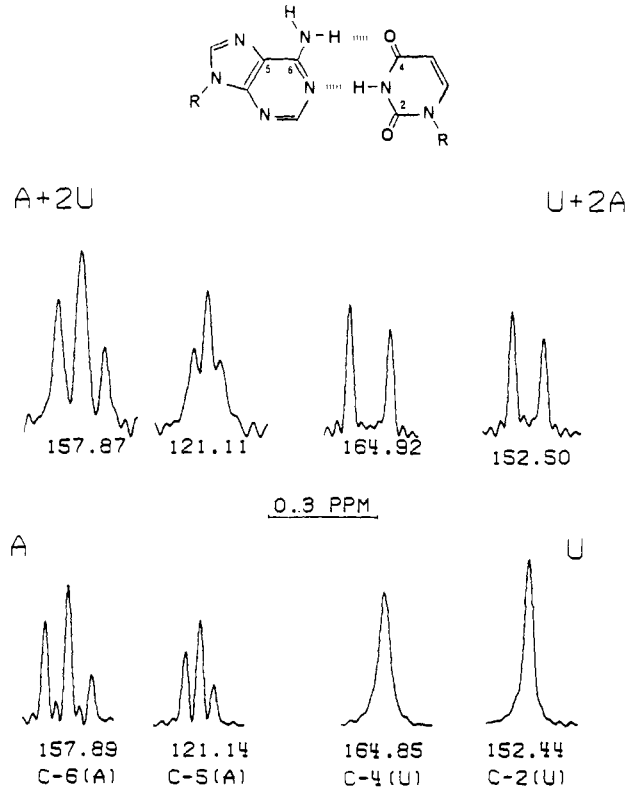
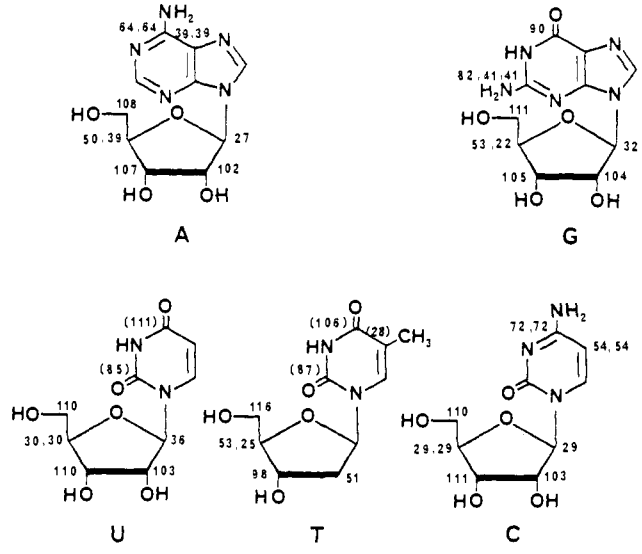


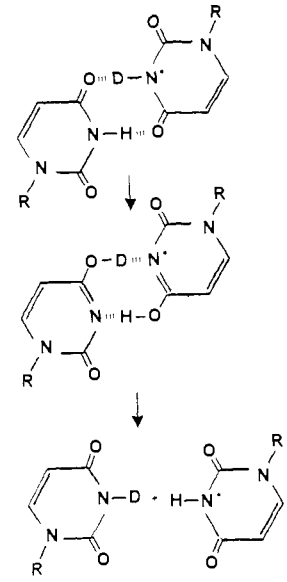
Figure 4. Isotopic multiplets of the base carbon-13 resonances of partially deuterated adenosine (A) and uridine (U) taken separately (bottom) and in their mixtures (top). The chemical shifts (in ppm) for the protio forms are listed under each band. The Watson–Crick base-pair structure is given.

Chart II. Deuterium Isotope Effects on Carbon-13 Chemical Shifts (in ppb) for Nucleosides



when 2 equiv of uridine is added to the adenosine solution. The behavior of the uridine resonances is more dramatic. None of the base resonances exhibited isotopic multiplets (C-2 and C-4 are shown in Figure 4) after the addition of a sufficient amount of CH_3OD to give an H/D ratio of ca. 1.2 for all of the exchangeable hydrogens. At the same time the expected multiplicities were observed for the ribose and methanol carbons. These results suggest that the imino hydrogens exchange rapidly in a process that does not involve the hydroxyls; i.e., the process is autocatalytic. When 2 equiv of adenosine is added to the uridine solution, the resonances of the base carbonyls split into doublets. Evidently, the engagement of the imino hydrogen in a Watson–Crick hydrogen bond (depicted in Figure 4)[20,21] inhibits the autocatalytic exchange process. One may envision the latter as involving uridine–uridine base pairing, hydrogen transfer within the pair, probably when each member is in the enol form, followed by separation and return to the keto form. This hypothetical mechanism is depicted in Scheme I. Three pieces of evidence can be cited in support of this mechanism. The self-association of uracil derivatives as well as thymine in chloroform solutions has been demonstrated by ^{13}C NMR spectroscopy.[13] The chemical shifts of carbons 2 and 4 were the most sensitive to this interaction.[13] Tautomerization of uracil derivatives has been demonstrated by UV spectroscopy.[22] Finally, the present results show that disruption of the uridine hydrogen-bonded dimer by formation of a more stable complex with adenosine leads in effect to inhibition of the exchange process. In fact, a titration of uridine with adenosine showed that a doublet structure of the C-2 and C-4 resonances of uridine could be discerned at an A/U ratio of 0.25. At this point, the rate of hydrogen exchange as estimated from the isotope shift is ca. 60 s^{-1}. Similar phenomena were observed with thymidine.

Scheme I. A Mechanism of Autocatalytic Hydrogen Isotope Exchange in Uridine

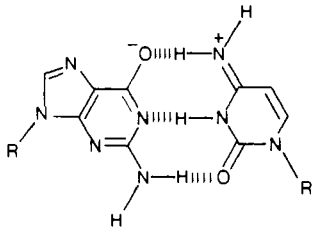


The carbon-13 resonances of those atoms of the guanosine and cytidine bases that exhibit isotopic multiplets are shown in Figure 5. Carbon 6 of guanosine is a doublet due to an isotope effect from the imino group. Carbon 2 is a quintet with spacings of 41 ppb due to $^2\Delta$ of 41 ppb from the amino group and $^2\Delta$ of 82 ppb from the imino group. Upon the addition of cytidine, the isotope effects due to the imino group are substantially reduced and almost disappear. The resonances of C-4 and C-5 of cytidine are triplets due to $^2\Delta$ and $^3\Delta$, respectively, from the amino group. Upon the addition of guanosine the triplets are transformed into broadened quartets, indicating that the amino hydrogens have become nonequivalent. The nonequivalence of the amino hydrogens of cytosine derivatives is a well-known phenomenon that occurs upon protonation[23] at N-3 or base pairing with guanidine derivatives.[24] Two main lines of interpretation of the present findings will be considered. In order to explain infrared spectral data on nucleoside

(20) A large body of evidence[21] indicates that, whenever possible, the association between the bases of nucleic acid components, including nucleosides, involves multiple hydrogen bonds. For the A–U and G–C systems the preference is for the formation of Watson–Crick base pairs. For convenience this approach was adopted in this paper in writing the structures of nucleoside dimers, although the results do not rule out other possible structures.

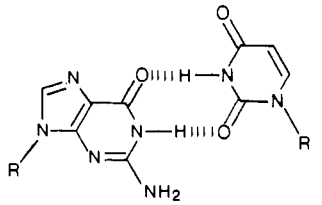
(21) Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: New York, 1984.
(22) Katritzky, A. R.; Waring, A. J. *J. Chem. Soc.* **1962**, 1540–1544.
(23) Miles, H. T.; Bradley, R. B.; Becker, E. D. *Science* **1963**, *142*, 1569–1571. Becker, E. D.; Miles, H. T.; Bradley, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 5575–5582.
(24) Shoup, R. R.; Miles, H. T.; Becker, E. D. *Biochem. Biophys. Res. Commun.* **1966**, *23*, 194–201.

pairs in crystals, Kyogoku et al.[25] proposed that the imino proton of guanosine is transferred across the hydrogen bond of the Watson–Crick pair leading to the protonation of cytidine, viz.[26]

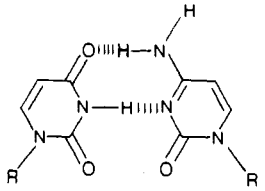


Such a proton transfer between guanosine and cytidine can account for the phenomena observed here. However, according to theoretical calculations, proton transfer within the guanosine–cytidine base pair is improbable.[27] An alternative and simpler interpretation of the present findings is that the NH···N hydrogen bond in the Watson–Crick G–C pair is much weaker than the hydrogen bond with the solvent leading to a substantial reduction in the isotope shift. At the same time the asymmetric hydrogen bonding of the NH_2 group of cytidine is sufficient to restrict the rotation about the C–N bond and render the hydrogens nonequivalent.

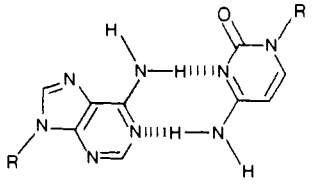
The following observations on solutions containing mixtures of noncomplementary (in the Watson–Crick sense) pairs of nucleosides support the above interpretations. The doublet structure of the C-4 and C-2 resonances of uridine was observed in the presence of guanosine. Apparently formation of the wobble G–U



pair competes with U–U association and effectively reduces the rate of the autocatalytic hydrogen exchange (see Scheme I). At the same time the multiplet structure of the C-6 and C-5 resonances of guanosine remained unaltered. The imino hydrogen of guanosine is now in an NH···O hydrogen bond as compared with the much weaker NH···N bond in the G–C pair. On the other hand, in mixtures of uridine and cytidine the base resonances of the former remained singlets, while the multiplet structure of the C-4 and C-5 resonances of the latter were modified in a way similar to that observed in G–C mixtures. These observations are consistent with the following structure of the U–C pair, although



they do not rule out proton transfer. Evidence supporting "simple" hydrogen bonding schemes and against proton-transfer structures comes from observations on adenosine–cytidine mixtures, in which an A–C pair may be formed. In these mixtures the multiplet



(25) Kyogoku, Y.; Tsuboi, M.; Shimanouchi, T.; Watanabe, I. *Nature (London)* **1961**, *189*, 120–122.

(26) Originally Kyogoku et al. placed the negative charge on N-1 of guanosine.[25]

(27) Clementi, E.; Mehl, J.; von Niessen, W. *J. Chem. Phys.* **1971**, *54*, 508–520.

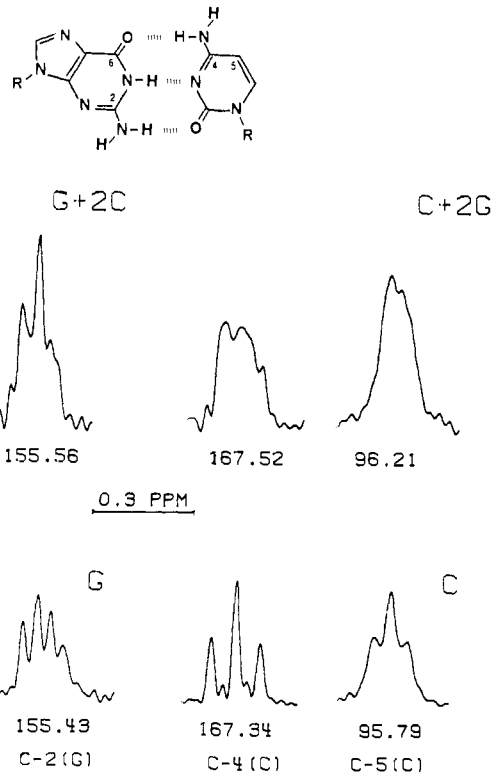


Figure 5. Isotopic multiplets of the base carbon-13 resonances of partially deuterated guanosine (G) and cytidine (C) taken separately (bottom) and in their mixtures (top). The chemical shifts (in ppm) for the protio forms are listed under each band. The Watson–Crick base-pair structure is given.

Table I. Estimates of Hydrogen Bond Energies in Watson–Crick Base Pairs

pair	carbon	$^2\Delta$, ppb	H bond	E, kcal/mol[a]
A–U	C-6(A)	64	HNH···O	3.83
	C-2(U)	85	NH···N	5.03 ± 0.39
	C-4(U)	111		
G–C	C-2(G)	57[b]	HNH···O	3.50
	C-6(G)	25	NH···N	1.15
	C-4(C)	71	HNH···O	4.13
		49		3.07

[a] Equation 7 was solved for E and the latter calculated by using the listed $^2\Delta$ values. [b] The experimental value was corrected to account for the interaction with the solvent.

structures of the C-4 and C-5 resonances of cytidine were modified in a fashion similar to that observed for G–C (see Figure 5) and C–U mixtures, while the multiplet structure of the C-6 and C-5 resonances of adenosine remained unchanged.

The energies of the individual hydrogen bonds in the Watson–Crick pairs can be estimated from the isotope effects by using eq 7. The results are summarized in Table I. Of the two values listed for C-4 of cytidine, the larger is similar to the one observed in the absence of base pairing and probably reflects interaction with the solvent. It should be emphasized that the values listed in Table I were obtained on the basis of empirical correlations and should be regarded as tentative. With these qualifications in mind, it is still of interest to observe that the sum of hydrogen bond energies for the A–U pair, which has two hydrogen bonds, is not smaller than that in the G–C pair, which has three. It is also noteworthy that the results (see Table I) for hydrogen bonds involving imino hydrogens are in agreement with hydrogen bond lengths obtained from crystal structure analyses of Watson–Crick base pairs in the self-complementary ApU[28] and GpC[29] systems.

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The shortest distance (2.82 Å) is for N-1(A)···N-3(U) and the longest (2.95 Å) for N-1(G)···N-3(C).

Conclusions

Partial deuteration of amino and imino groups in conjugated systems leads to isotope effects on carbon-13 chemical shifts and multiplet structure of the resonances of atoms bearing such groups as well as of the resonances of vicinal atoms. In aniline derivatives the isotope effects are larger for groups involved in intramolecular hydrogen bonds. Empirical expressions relate isotope effects with amino proton chemical shifts and hydrogen bond energies. These expressions can be useful for spectral assignments of the corresponding proton and carbon-13 resonances and for estimating hydrogen bond energies. The isotopic multiplets in the base resonances of nucleosides are modified upon base-pairing through intermolecular hydrogen bonds. Intimate details regarding hydrogen isotope exchange and relative hydrogen bond energies are thus revealed. The approach of isotopic multiplets should be applicable to the study of duplexes of oligonucleotides (in aqueous solutions), for which slow proton exchange has been demonstrated by proton NMR spectroscopy.[30]

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Photophysics of the Intramolecular Exciplex Formation in ω-(1-Pyrenyl)-α-*N*,*N*-dimethylaminoalkanes

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Abstract: The photophysical properties of ω-(1-pyrenyl)-α-*N*,*N*-dimethylaminoethane, -propane, -butane, and -octane are investigated. Excitation of the pyrene chromophore leads, in solvents of medium polarity, to the formation of an intramolecular exciplex, but the compounds with four and eight methylene groups in the alkyl chain do not show exciplex emission. The dipole moment and the emission energy of the exciplex decrease with increasing chain length. The kinetics of exciplex formation are analyzed in solvents of medium polarity using time-correlated fluorescence measurements. These results indicate that intramolecular exciplex formation in these compounds cannot be considered as the monomolecular analogue of intermolecular exciplex formation, but must be interpreted in the framework of rotational isomerism. The influence of the chain length on the exciplex formation process is evaluated. In polar solvents, such as acetonitrile, no exciplex emission is observed except for the compound with an ethyl chain. The standard free enthalpy of the radical ion pair is in this solvent some 10 kJ mol^{-1} lower than the standard free enthalpy of the intramolecular exciplex. The formation of the ion-pair state has been confirmed by picosecond transient absorption spectroscopy.

Complex formation in the excited state, in which the acceptor is an aromatic hydrocarbon molecule and the donor an amine (aromatic or aliphatic), has received substantial attention.[1-4]

Classically the kinetics of intermolecular exciplex formation can be described by Scheme I.[5,6]

Within the framework of this scheme the following equations for fluorescence quantum yields and fluorescence decay parameters can be derived.

$$\frac{\Phi_E}{\Phi_A} = \frac{k_5}{k_1}\frac{k_3}{Y}[D] \quad (1)$$

$$I_A(t) \approx \frac{k_1(\lambda_2 - X)}{\lambda_2 - \lambda_1}\{\exp(-\lambda_1 t) + C\exp(-\lambda_2 t)\} \quad (2)$$

$$I_E(t) \approx \frac{k_5 k_3[D]}{\lambda_2 - \lambda_1}\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \quad (3)$$

$$\lambda_{2,1} = \tfrac{1}{2}\{(X + Y) \pm ((X - Y)^2 + 4k_3k_4[D])^{1/2}\} \quad (4)$$

$$C = (X - \lambda_1)/(\lambda_2 - X) \quad (5)$$

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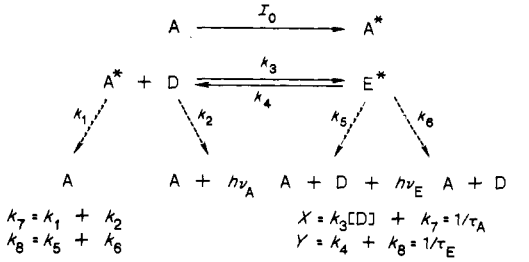
Scheme I



At temperatures where k_4 is much smaller than k_8, these equations simplify to

$$\frac{\Phi_E}{\Phi_A} = \frac{k_5}{k_1}\frac{k_3}{k_8}[D] \quad (6)$$

$$I_A(t) \approx k_1 \exp(-\lambda_2 t) \quad (7)$$

$$I_E(t) \approx \frac{k_5 k_3[D]}{\lambda_2 - \lambda_1}\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \quad (8)$$

$$\lambda_1 = Y \quad (9)$$

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