stronger than in the two homocyclic compounds. The consequent narrowing of the C(1)–C(11)–C(6) angle, 95.5 (4)° in **2** vs. 99.6 (3)° in **3** and 101.0 (3)° in **4**, is enhanced by the lengthening of the bridge C–C bonds [average value 1.488 (8) Å in **2**, to be compared with 1.477 (9) Å in **3** and 1.470 (4) Å in **4**].

Supplementary Material Available: Tables of final atomic parameters and a list of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Definitive Theoretical Evidence for the Nonplanarity of the Hydronium Ion (H_3O^+)

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In recent communications to this journal,[1,2] there has been debate, on the basis of ^{17}O NMR data, as to whether the hydronium ion (H_3O^+) is planar[1] or pyramidal.[2] Both of these communications[1,2] claimed that ab initio calculations supported a planar structure for H_3O^+. In fact, the best ab initio calculations available at the time indicated a nonplanar structure.[3-5] In this communication, we draw attention to this fact and provide further, definitive theoretical evidence for the nonplanarity of H_3O^+. In the process, we also present theoretical data for the effect of electron correlation on the calculated structure and inversion barrier of ammonia.

Our strategy is to carry out initially calculations for ammonia, for which the experimental situation is reasonably clear cut,[6] at a level of theory sufficiently high so as to produce quantitatively accurate results. We then use this level of theory to make predictions for the less well-established case of H_3O^+.

We have previously reported[7] near Hartree–Fock limit calculations for ammonia. The present calculations were carried out with the same large basis set.[8] Electron correlation was incorporated using Møller–Plesset perturbation theory[9] terminated at second (MP2) and third (MP3) order. Calculations were carried out by using modified versions[10] of the ATMOL3[11] and SCEP[12] programs. Theoretical structures, total energies, and inversion barriers are shown for NH_3 and H_3O^+ in Tables I and II, respectively.

Table I. Optimized Structural and Energy Data for Pyramidal (C_{3v}) and Planar (D_{3h}) Forms of Ammonia[a]

	Hartree–Fock[b]	MP2	MP3	exptl[c]
r(N–H) (C_{3v})	0.999	1.009	1.007	1.012
∠HNH (C_{3v})	107.7	106.9	106.9	106.7
r(N–H) (D_{3h})	0.984	0.993	0.991	
E (C_{3v})	−56.22333	−56.44310	−56.45312	
E (D_{3h})	−56.21504	−56.43450	−56.44423	
barrier	5.2	5.4	5.6	5.8

[a] Bond lengths are given in angstroms, bond angles in degrees, total energies in hartrees, relative energies (barriers) in kilocalories/mole. [b] From ref 7. [c] From ref 6.

Table II. Optimized Structural and Energy Data for Pyramidal (C_{3v}) and Planar (D_{3h}) Forms of H_3O^+[a]

	Hartree–Fock	MP2	MP3
r(O–H) (C_{3v})	0.960	0.977	0.973
∠HOH (C_{3v})	113.2	111.2	111.6
r(O–H) (D_{3h})	0.955	0.969	0.965
E (C_{3v})	−76.34503	−76.57987	−76.58579
E (D_{3h})	−76.34261	−76.57603	−76.58212
barrier	1.5	2.4	2.3

[a] Units as in Table I.

For ammonia, the previously reported Hartree–Fock structure[7] is significantly improved at the MP2 and MP3 correlation levels. The calculated N–H length in the equilibrium structure is slightly shorter than the experimental value, a result consistent with corresponding calculations for H_2O.[13] The main quantities of concern in the present study, namely, the HNH bond angle and the inversion barrier, are well reproduced by our best (MP3) calculations: 106.9° and 5.6 kcal mol^{-1} vs. experimental values of 106.7° and 5.8 kcal mol^{-1}, respectively. This lends confidence to the reliability of our predictions at the same theoretical level for H_3O^+. The small positive contribution (0.4 kcal mol^{-1}) of electron correlation to the inversion barrier in ammonia is similar to values noted previously (0.4[3c] and 0.35[14] kcal mol^{-1}). We are unaware of any previous use of basis sets as large as those used here in studies of the effect of electron correlation on the structure of ammonia.

Our results for H_3O^+ (Table II) show a substantially greater contribution of electron correlation to both the structure and inversion barrier, in agreement with previous studies.[3,5] Our best calculations indicate a pyramidal equilibrium structure with an O–H length of 0.973 Å,[15] HOH bond angle of 111.6°, and inversion barrier of 2.3 kcal mol^{-1}. The structure is similar to that of the previous best studies, carried out with somewhat smaller basis sets.[3a,g,5] On the other hand, our inversion barrier is higher than previous best estimates (1.5–2.0 kcal mol^{-1}).[3c,g,5] This difference may be attributed almost totally to the Hartree–Fock component of the calculation in that the correlation contribution to the barrier in our study (0.8 kcal mol^{-1}) is similar to the values obtained previously (0.7–0.8 kcal mol^{-1}).[3c,g,5] Because our basis set is larger than those used previously, we believe our predicted barrier to be the most reliable value available to date. The calculations thus leave no room for doubt in concluding that H_3O^+

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(1) Mateescu, G. C.; Benedikt, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 3959.

(2) Symons, M. C. R. *J. Am. Chem. Soc.* **1980**, *102*, 3982.

(3) See, for example: (a) Lischka, H.; Dyczmons, V. *Chem. Phys. Lett.* **1973**, *23*, 167. (b) Almlof, J.; Wahlgren, U. *Theor. Chim. Acta* **1973**, *28*, 161. (c) Ahlrichs, R.; Driessler, F.; Lischka, H; Staemmler, V.; Kutzelnigg, W. *J. Chem. Phys* **1975**, *62*, 1235; (d) Kollman, P. A.; Bender, C. F. *Chem. Phys. Lett.* **1973**, *21*, 271. (e) Delpuech, J. J.; Serratrice, G.; Strich, A.; Veillard, A. *Mol. Phys.* **1975**, *29*, 849. (f) Hariharan, P. C.; Pople, J. A. *Ibid.* **1974**, *27*, 209. (g) Diercksen, G. H.; Kraemer, W.; Roos, B. O. *Theor. Chim. Acta* **1975**, *36*, 249.

(4) Poorer quality calculations (extended basis sets without polarization functions) yield planar or near-planar structures: (a) Newton, M. D.; Ehrenson, S. *J. Am. Chem. Soc.* **1971**, *93*, 4971; (b) Lathan, W. A.; Hehre, W. J.; Curtiss, L. A.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 6377. (c) Moskowitz, J. W.; Harrison, M. C. *J. Chem. Phys.* **1965**, *43*, 3550. (d) Kollman, P. A.; Allen, L. C. *J. Am. Chem. Soc.* **1970**, *92*, 6101.

(5) More recent calculations include Ferguson, W. I.; Handy, N. C. *Chem. Phys. Lett.* **1980**, *71*, 95.

(6) (a) Kuchitsu, K.; Guillory, J. P.; Bartell, L. S. *J. Chem. Phys.* **1968**, *49*, 2488. (b) Swalen, J. D.; Ibers, J. A. *Ibid.* **1962**, *36*, 1914.

(7) Rodwell, W. R.; Radom, L. *J. Chem. Phys.* **1980**, *72*, 2205.

(8) (a) The (13s 8p/8s) primitive atomic Gaussian basis set of van Duijneveldt[8b] was contracted to [8s 5p/5s] by grouping together only the innermost six s and four p functions for nitrogen and oxygen, and four s primitive functions for each hydrogen, into single contracted functions. This set of functions was augmented by two sets of d-polarization functions for nitrogen and oxygen ($\zeta_d = 1.50, 0.35$), and two sets of p-polarization functions for each hydrogen ($\zeta_p = 1.40, 0.25$), giving a total of 66 contracted functions for each of NH_3 and H_3O^+. (b) van Duijneveldt, F. B. IBM Technical Research Report RJ 945 (No. 16437), Dec 1971.

(9) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545.

(10) Rodwell, W. R., unpublished.

(11) Saunders, V. R.; Guest, M. F. "ATMOL3 Users Guide"; Science Research Council: Daresbury, England.

(12) Dykstra, C. E. *QCPE* **1978**, *11*, 346.

(13) (a) Bartlett, R. J.; Shavitt, I.; Purviss, G. D. *J. Chem. Phys.* **1979**, *71*, 281. (b) The shortness of the bond length is shown to be a correlation rather than a basis-set deficiency, and the error is removed on moving to higher levels of correlation theory.

(14) Stevens, R. M. *J. Chem. Phys.* **1974**, *61*, 2086.

(15) On the basis of our results for NH_3 and previous results for H_2O, we would expect that this value is an underestimate and that the experimental length is likely to be approximately 0.98 Å.

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has a pyramidal equilibrium geometry. We predict a bond angle of 111.6° and an inversion barrier of 2.3 kcal mol^{-1}. These results are consistent with recent neutron diffraction findings in the solid state (yielding HOH bond angles of 110.4° for p-$CH_3C_6H_4SO_3^-H_3O^+$ and 112.7° for $F_3CSO_3^-H_3O^+$),[16] and Symons' interpretation of the ^{17}O NMR spectrum of H_3O^+ (yielding a bond angle of 111.3°).[2]

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[16] (a) Lundgren, J. O.; Williams, J. M. *J. Chem. Phys.* **1973**, *58*, 788. (b) Lundgren, J. O.; Olovsson, I. In "The Hydrogen Bond", Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; Vol. II.

Triplet GpCpA Forms a Stable RNA Duplex

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Perfect RNA duplexes containing three Watson–Crick base pairs are unstable under physiological conditions.[1] Triribonucleotides, however, can form stable duplexes with single stranded helical regions, such as in tRNA loops where the bases already stacked in the helix account for this enhanced stability.[2] An alternate means of increasing base stacking and thus strengthening overall duplexes is the presence of dangling bases.[3] We report the first triribonucleotide to form a simple stable duplex, GpCpA:GpCpA, which contains two G·C Watson–Crick base pairs and two 3′-dangling adenosines. This duplex is similar in stability to the corresponding self-complementary tetramer duplex, formed from UpGpCpA, which contains four Watson–Crick pairs, and must derive its stability over the dinucleotide duplex GpC:GpC by virtue of its 3′-dangling adenosine residues whose contributions to duplex stability approximate those of A·U pairs.

Oligoribonucleotides, GpC, GpCpA, GpCpApA, and ApGpC, were synthesized by using a phosphotriester method.[4] Variable-temperature ^1H nuclear magnetic resonance spectroscopy was used to monitor duplex stability. The chemical shift vs. temperature changes for the aromatic and ribose H-1′ protons of GpCpA are shown in Figure 1 and listed in Table I. The averaged T_m for the sigmoidal plots of these protons is 33 °C at 7.3 mM. The plots displayed in Figure 1 are only consistent with a GpCpA duplex containing two Watson–Crick base pairs. The chemical shift of CH-5 changes by 0.615 ppm to higher field over the temperature range 70–10 °C, and this upfield movement is characteristic of a CH-5 on a cytidine which is involved in a normal G·C Watson–Crick base pair as is shown by the 0.559-ppm upfield shift for the CH-5 in the UGCA duplex (see Table II). Protons, AH-8 and AH-2, of the dangling adenosines exhibit pronounced upfield chemical shift changes during GpCpA duplex formation. In addition, the $J_{1',2'}$ coupling constants for the ribose H-1′ protons of the guanosine and cytidine residues collapse to <0.5 Hz below 30 °C, while the $J_{1',2'}$ values for adenosine decrease but do not become <0.5 Hz until close to O °C. This is indicative of strong GC stacking, while the 3′-adenosine unit still retains some flexibility in the duplex.[5]

Although the trimer, GpCpA, contains a purine–pyrimidine–purine sequence, these results provide an interesting contrast to those obtained from studies of similar type of base sequence which preferred internal bulge base conformations[6] at lower temperatures.

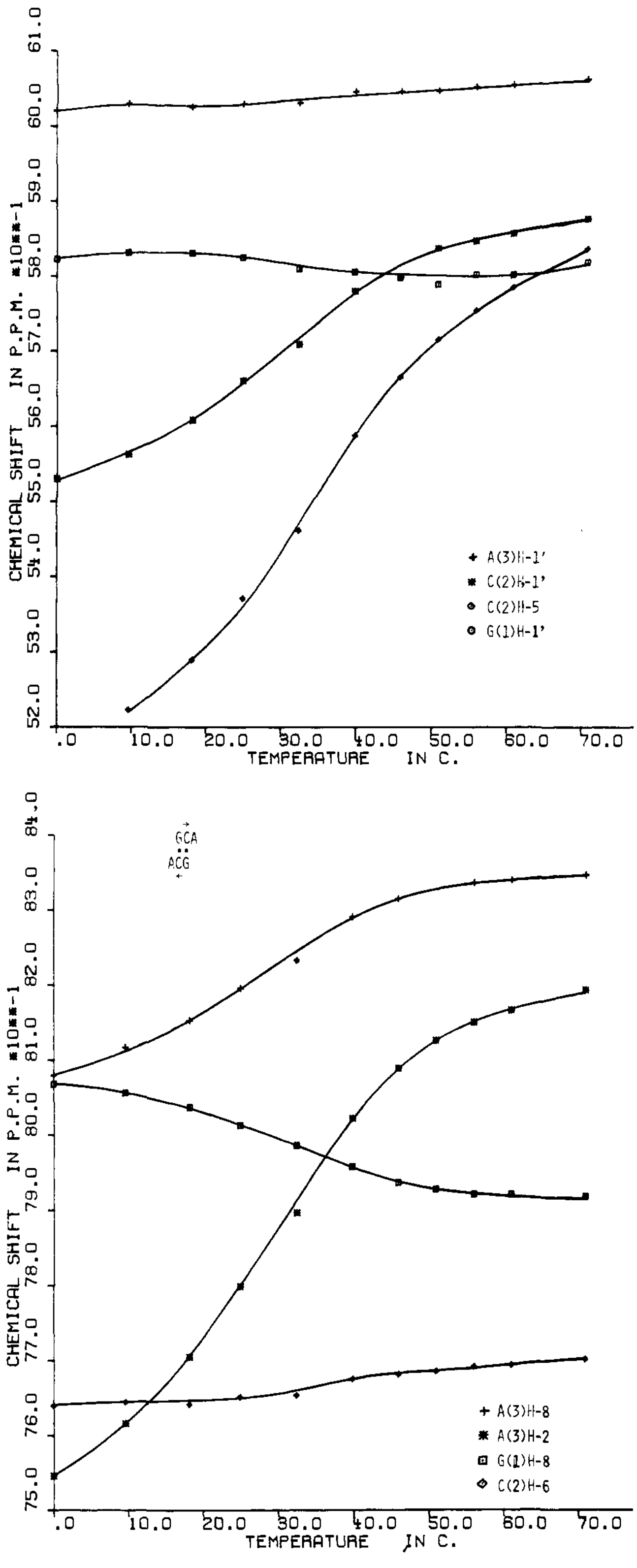

Figure 1. Chemical shift vs. temperature plots for GpCpA at 7.3 mM. Sample was dissolved in 100% D_2O containing 0.01 M sodium phosphate buffer (pD 7.0) and 1.0 M sodium chloride.

The spectacular stability of the GpCpA duplex containing a 3′-dangling adenosine is even more dramatic when compared to the trinucleotide ApGpC containing a 5′-dangling adenosine.

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[1] (a) Brahms, J.; Aubertin, A. M.; Dirheimer, G.; Grunberg-Manago, M. *Biochemistry* **1969**, *8*, 3269–3277. (b) Jaskunas, S. R.; Cantor, C. R.; Tinoco, I. Jr., *Ibid.* **1968**, *7*, 3164–3178. (c) Borer, P. N.; Dengler, B.; Tinoco, I., Jr.; Uhlenbeck, O. C. *J. Mol. Biol.* **1974**, *86*, 843.

[2] (a) Uhlenbeck, O. C.; Baller, J.; Doty, P. *Nature (London)* **1970**, *225*, 508–510. (b) Grosjean, H. J.; de Henau, S.; Crothers, D. M. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 610–614 and references therein.

[3] (a) Martin, F. H.; Uhlenbeck, O. C.; Doty, P. *J. Mol. Biol.* **1971**, *57*, 201. (b) Neilson, T.; Romaniuk, P. J.; Alkema, D.; Everett, J. R.; Hughes, D. W.; Bell, R. A. *Nucleic* Acids Res. *Spec. Publ.* **1980**, *No. 7*, 293–311.

[4] Werstiuk, E. S.; Neilson, T. *Can. J. Chem.* **1976**, *54*, 2689–2696.

[5] Cheng, D. M.; Danyluk, S. S.; Dhingra, M. M.; Ezra, F. S.; MacCoss, M.; Mitra, C. K.; Sarma, R. H. *Biochemistry* **1980**, *19*, 2491–2497 and references therein.

[6] Lee, C.-H.; Tinoco, I., Jr., *Biophys. Chem.* **1980**, *11*, 283–294.

0002-7863/81/1503-2866$01.25/0