Figure 1. A plot of (R_p)-1 showing thermal ellipsoids of the atoms at the 50% probability level.[10]

The adenin-9-yl residue is fairly planar and exists in an anti conformation relative to the ribose [κ_{CN} = O(1')–C(1')–N(9)–C(4) = –98.1 (8)°].[11] Ribose puckering is a characteristic C(4')-*exo*,C(3')-*endo*.[12] The orientation of the C(5')–O(5') bond is trans, gauche [∠O(5')–C(5')–C(4')–O(1') = 179.7 (6)°].[11] Due to the presence of a hydrating water in the crystal lattice, the molecules of 1 are linked via hydrogen bonds: OP–OW[i], 2.722 Å; NP–OW[ii], 2.89 Å; N(1)–OW[iii], 2.87 Å; N(6)–OW, 3.20 Å.

The unambiguous assignment of absolute configuration at phosphorus as (R_p)-1 prompted us to synthesize the diastereomers of 2'-deoxyadenosine cyclic 3',5'-[^{15}N]phosphoranilidate. Their synthesis was achieved by treatment of the triethylammonium salt of cdAMP with Ph₃P–CCl₄–[^{15}N]aniline.[13] (S_p)-1: R_f 0.33 [CHCl₃–EtOH (85:15)], ³¹P NMR (C₅H₅N, downfield from H₃PO₄) δ +0.74, $^1J_{P^{-15}N}$ = 47.4 Hz; (R_p)-1: R_f 0.27, ³¹P NMR (C₅H₅N, upfield from H₃PO₄) δ –3.21, $^1J_{P^{-15}N}$ = 36.7 Hz. The values of the direct spin–spin coupling constant $^1J_{P^{-15}N}$ fulfill the empirical rule: "For the pair of diastereomeric chair-shaped 1,3,2-dioxaphosphorinanes the direct spin–spin coupling constant between phosphorus and exocyclic magnetically active X (I = $^1/_2$; ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{77}Se) depends on the spatial orientation of X. $^1J_{P-X}$ acquires a lower absolute value for the isomer with the axially oriented X than for the one having X in the equatorial position".[2d,3,14]

$$|^1J_{P-X}|_{ax} < |^1J_{P-X}|_{eq}$$

In the light of recent work by Bentrude and Sopchik,[15] the correlation of the phosphorus configuration with $|^1J_{^{15}NP}|$ appears also valid even through one of diastereomeric forms of thymidine cyclic 3',5'-phosphordimethylamidate[16] exists in solution largely in the nonchair dioxaphosphorinane conformation.

Other than the fundamental information about the solid-state structure of (R_p)-1, the precursor of 2'-deoxyadenosine cyclic 3',5'-[^{18}O]phosphate[5c] and -phosphorothioate,[2b] this work clearly demonstrates the applicability of heteronuclear magnetic resonance for the unambiguous configurational assignments at the phos-

phorus atom in the diastereomeric 2-arylamino-2-oxo-1,3,2-dioxaphosphorinanes.

Molecular Structure of 10-Bromo-1,6-methano-2-aza[10]annulene[1]

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The new heterocyclic system 1,6-methano-2-aza[10]annulene (**1**), recently synthesized by Vogel et al.,[2] qualifies as an aromatic 10π analogue of pyridine in spectroscopic and—to some extent—chemical respects. A crystalline bromo substitution product of **1**, tentatively assigned the structure of 10-bromo-
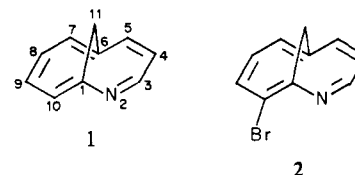
1,6-methano-2-aza[10]annulene (**2**), is obtained by successive treatment of **1** with bromine and the base 1,5-diazabicyclo-[4.3.0]non-5-ene (addition–elimination mechanism).[3]

As reported here, the X-ray structure analysis of this compound not only confirmed the formation of **2** but also allowed the full

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(12) Chwang, A. K.; Sundaralingam, M. *Acta Crystallogr., Sect. B* **1974**, *B30*, 1233.

(13) Essentially the same procedure as described under ref 8 was applied by using [^{15}N]aniline, isotopic enrichment 52%.

(14) (a) Stec, W. J.; *Z. Naturforsch. B* **1974**, *29B*, 109. (b) Stec, W. J.; Kinas, R. W.; Okruszek, A. *Ibid.* **1976**, *31B*, 393.

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(1) Systematic name 3-bromo-2,7-methanoaza[10]annulene; the above nomenclature is used in order to avoid confusion in structural comparisons with bridged [10]annulenes.

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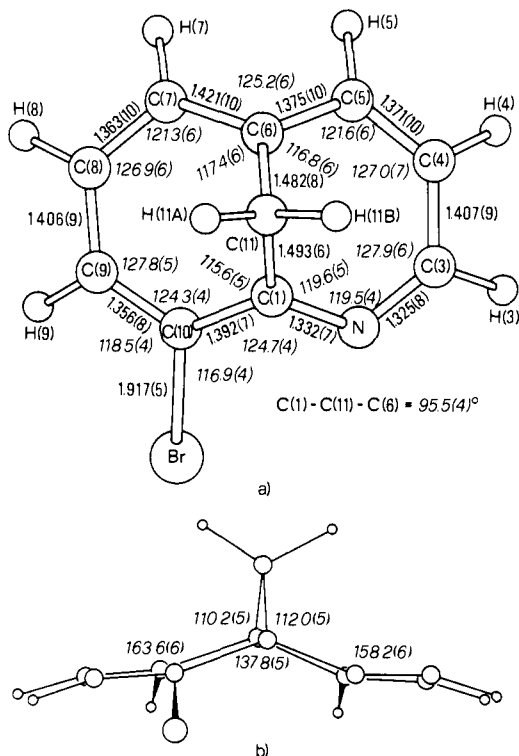
Figure 1. The molecule of **2** viewed along two principal axes of inertia, when unit weight is given to all the atoms. (a) Numbering scheme and bond distances and angles involving nonhydrogen atoms. (b) Dihedral angles.

characterization of the geometry of the 1,6-methano-2-aza[10]-annulene framework.

Crystal data of the substance under study at room temperature are a = 12.007 (2), b = 10.135 (1), c = 7.249 (1) Å; β = 93.69 (2)°; U = 880.3 Å³; Z = 4; monoclinic, space group $P2_1/c$; μ(Mo Kα) = 48.85 cm^{-1}; ρ_{calcd} = 1.676, ρ_{measd} = 1.673 g cm^{-3} (flotation). A prism of approximate dimensions 0.32 × 0.21 × 0.07 mm was used for cell parameter and intensity measurements. The data collection was carried out on a computer-controlled diffractometer by using graphite-monochromated Mo Kα radiation (λ 0.7107 Å). Intensities were measured by variable rate θ–2θ scans within a θ sphere of 23.5°. Three standard reflections were monitored after every 47 intensity measurements; they showed no significant drift in intensity. Most of the accessible diffraction maxima (89%) were recorded twice, at different Ψ values. Of the 1307 independent reflections collected, a total of 1205 with $I > 0$ were retained and were corrected for Lorentz, polarization, background, and absorption[4] effects. Standard Patterson and Fourier techniques led to an electron density map on which the bond distances, as well as the relative heights of the peaks, were consistent with structure **2**.[5] H-atom positions were derived from difference maps in the course of the refinement, which was by full-matrix least-squares minimization of the quantity $\sum w(\Delta F)^2$, with weights w = $4F_o^2/\sigma^2(F_o^2)$. In the final cycles, 141 parameters were simultaneously adjusted: coordinates and anisotropic temperature coefficients b_{ij} for Br, C, and N atoms, coordinates and isotropic B's for the 8 H atoms, and a scale factor.[6] The resulting atomic

parameters are given in Tables I and II;[7] observed and calculated structure factors are listed in Table III.[7] The final R^8 was 0.054 [0.035 on 878 reflections with $F^2 > 2\sigma(F^2)$], and the weighted Rw^9 was 0.038. The goodness of fit, on the basis of 1205 weighted reflections and 141 parameters, was 1.05. A final difference map showed a residue of 0.9 eÅ^{-3} located $\sim$1 Å away from the Br atom.

A schematic representation of the molecule is shown in Figure 1, where bond distances and angles involving nonhydrogen atoms are reported. C–H bond lengths are in the range 0.92–1.08 Å (mean 1.01 Å, esd's about 0.05 Å); no unusual values for the angles involving the H atoms are present in the molecule. Since there are no intermolecular contacts less than the sum of van der Waals radii (C 1.7, N 1.6, Br 1.95, H 1.1 Å), the geometry reported in Figure 1 can be assumed, to a first approximation, as that of the isolated molecule.

The virtual equivalence of the two C–N bond lengths is clearly indicative of delocalization. Their values are somewhat smaller than in pyridine[10] [1.340 (5) Å] and 2-aminopyridine[11] [1.345 (2) and 1.340 (2) Å] but similar to those found in 3,5-dinitro-pyridine[12] [1.330 (3) and 1.327 (4) Å] and 3-aminopyridine[13] [1.336 (4) and 1.331 (5) Å]. In all these molecules the angle at N varies between 116.8° (pyridine[10]) and 117.7° (2-amino-pyridine[11]), while in **2** it is enlarged to 119.5 (4)°. Yet, this value is smaller, by at least 2°, than that usually found at the ring C atoms directly bound to C(1) and C(6) in [10] annulenes. For example, the smallest value for this angle is 121.7 (2)° in 1,6-methano[10]annulene-2-carboxylic acid (**3**)[14] and 123.8 (3)° in 11,11-difluoro-1,6-methano[10]annulene (**4**).[15] With respect to the latter two systems, other significant differences in the geometrical features are (i) the short bond distance C(5)–C(6), 1.375(10) Å, compared with a minimum value of 1.397 (10) Å in **3** and 1.399 (4) Å in **4** for ring C–C bonds involving the bridge atoms C(1) and C(6) and (ii) the large value of the angle N–C-(1)–C(11), 119.6(5)°, which exceeds by more than 2° the largest of the corresponding angles at C(1) and/or C(6) in **3** [117.0 (3)°] and **4** [117.3 (2)°].

That the presence of the N atom implies relevant distortions in the annulene ring is also documented by the lack of coplanarity for atoms C(1), N, C(5), and C(6) (plane A) and, to a lesser extent, for atoms N, C(3), C(4), and C(5) (plane B). Indeed, displacements up to 0.019 Å (>3 esd's) from plane A are observed for atoms C(5) and C(6), while atom C(4) is displaced from plane B by 0.012 Å ($\sim$2 esd's). By contrast, strict coplanarity is maintained by the corresponding atoms in the other "half" of the annulene system [C(1), C(6), C(7), and C(10), plane C; C(7), C(8), C(9), and C(10), plane D], where displacements do not exceed 1 esd. Furthermore, the dihedral angle between planes A and B, 158.2 (6)°, is significantly different from that between planes C and D, 163.6 (6)°.

Finally, a remarkable feature of structure **2** is the value of the transannular distance C(1)···C(6), 2.202 (7) Å, about 0.06 Å shorter than in **3** [2.26 (1) Å] and **4** [2.269 (4) Å] and suggesting that the interaction between the two atoms is here somewhat

(4) A locally (Milan) modified version of program ORABS (Wehe, D. J.; Busing, W. R.; Levy, H. A. Report ORNL-TM-229, Oak Ridge National Laboratory, Tennessee, 1962, was used. Transmission factors are in the range 0.33–0.71. To test the reliability of the applied correction, eight selected reflections were monitored at several Ψ values, for a total of 113 measurements. Observed discrepancies among equivalent reflections, up to 53%, reduced to 5% after absorption correction.

(5) Attempts were also made to interpret the map according to the other possible product of the bromo substitution of **1**, namely, 7-bromo-1,6-methano-2-aza[10]annulene. The structure of the latter compound can formally be obtained by interchanging atoms N and C(5) of its isomer (**2**). After few cycles of least-squares refinement, anomalous values of the temperature factors and geometrical arguments ruled out this alternative interpretation.

(6) Atomic form factors for C, N, and Br were from: Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104. For H the atomic form factors were from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175. The Br form factor was decreased by 0.374 to take into account the real component of anomalous dispersion ("International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. IV, p 149.

(7) See paragraph at the end of the paper regarding supplementary material.

(8) $R = \sum\lVert F_o\rvert - \lvert F_c\rVert/\sum\lvert F_o\rvert$

(9) $Rw = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w(F_o)^2]^{1/2}$

(10) Microwave results by: Bak, B.; Hansen-Nygaard, L.; Rastrup-Andersen, J. *J. Mol. Spectrosc.* **1958**, *2*, 361.

(11) Chao, M.; Schempp, E.; Rosenstein, R. D. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2922.

(12) Destro, R.; Pilati, T.; Simonetta, M. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2071.

(13) Chao, M.; Schempp, E.; Rosenstein, R. D. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2924.

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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 (H₃O⁺)

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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 (H₃O⁺) is planar[1] or pyramidal.[2] Both of these communications[1,2] claimed that ab initio calculations supported a planar structure for H₃O⁺. 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 H₃O⁺. 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 H₃O⁺.

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 NH₃ and H₃O⁺ in Tables I and II, respectively.

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 H₂O.[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 H₃O⁺. 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 H₃O⁺ (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 H₃O⁺

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 H₃O⁺[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.

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