stand for 48 hr at 25°. After distilling off solvent under vacuum, I was recovered in quantitative yield, mp 109–111°, not depressed by mixture with authentic pure trityl chloride, carbon and hydrogen both correct within 0.25%. Even when trityl chloride and bromide were refluxed with pyridine for 48 hr under nitrogen in benzene solution or in the absence of benzene, the unreacted halides were recovered quantitatively. When the mixtures were heated in sealed tubes at 150–200° for 48 hr, unreacted halides and tarlike material were isolated.

Isolation and Physical Properties of II. A benzene solution (200 ml) of trityl chloride (0.3 *M*) and pyridine (0.5 *M*) was allowed to stand for several days at room temperature. The prismatic fine crystalline material (0.010 g) obtained from the solution was filtered, washed three times with dry benzene, and dried in a desiccator under reduced pressure, mp 177.5° without decomposition.

Anal. Calcd for $C_{24}H_{22}NOCl$: C, 76.68; H, 5.90; N, 3.73; Cl, 9.43. Found: C 76.51; H, 5.48; N, 3.98; Cl, 9.15.

A Perkin-Elmer Model 21 double beam spectrophotometer was used to measure the infrared spectra in chloroform, potassium bromide pellet, and Nujol mull. No C–N$^+$ peak analogous to that in benzylpyridinium chloride could be detected.

X-Ray analysis of the crystalline material, mp 177.5°, was attempted.[19] Preliminary data showed that the crystal was triclinic with a measured density (Berman balance using toluene) of 1.252 g/ml. The unit cell volume is about 988 Å^3 and, assuming two molecules per unit cell, the density is 1.26 g/ml.

Decomposition of II. The crystalline material (mp 176.5°) synthesized from trityl chloride and pyridinium chloride (1.5 g) was heated gradually to 200–250° under 0.2–0.3 mm. A white solid material condensed on the cold part of the glass apparatus, while liquid material was collected farther on in a cold trap (−78°).

Water was detected as a part of the liquid by reaction with calcium hydride and cupric sulfate. After drying the liquid over Drierite, pyridine was identified as another component by infrared. The melting point of the white solid was 105–110° before and 110–112° after recrystallization from *n*-hexane. There was no depression when the compound was mixed with pure trityl chloride, and this solid was identified as trityl chloride also by infrared spectrum.

The crystalline material (0.1 g) was mixed with 1 ml of water at room temperature (heterogeneous). After the aqueous solution was filtered, the insoluble white solid was washed with water and ethyl alcohol. It melted at 160–161°, and showed no depression on mixing with pure triphenylcarbinol (161–162°). The infrared spectrum of the white solid in chloroform solution was identical with that of pure triphenylcarbinol. The crystalline material (0.1 g) was dissolved in 5 ml of absolute methyl alcohol and allowed to stand overnight. After distilling off the solvent (4 ml), solid material precipitated from the solution upon cooling. The compound was isolated and washed with methyl alcohol, mp 83–84°. No depression was found on mixing it with pure trityl methyl ether (84°) prepared from a methyl alcohol solution of trityl chloride and pyridine. The infrared spectra were superimposable.

Other Molecular Complexes of Triphenylcarbinol or Pyridinium Chloride. A chloroform solution (20 ml) of 1.8 g of benzhydrol and 1.2 g of pyridinium chloride was prepared and allowed to stand overnight. When part of the chloroform (17 ml) was distilled off and the solution cooled, white crystalline material precipitated, mp 95–96°.

Anal. Calcd for $C_{18}H_{18}NOCl$: C, 72.11; H, 6.05; N, 4.67; Cl, 11.83. Found: C, 71.68; H, 5.82; N, 4.46; Cl, 11.96. From triphenylcarbinol and 2,6-lutidinium chloride, a complex compound was obtained, mp 199°.

Anal. Calcd for $C_{26}H_{26}NOCl$: C, 77.30; H, 6.49; N, 3.47; Cl, 8.78. Found: C, 77.12; H, 6.56; N, 3.60; Cl, 8.62.

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[19] The X-ray studies were performed by Dr. Jerry Silverman, Air Force Cambridge Research Laboratories.

Covalent Addition of Bisulfite Ion to 2-Amino-1-methylpyrimidinium Ion

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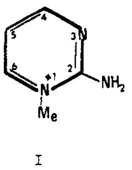
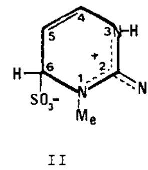
Contribution from the School of Pharmacy, University of Kansas, Lawrence, Kansas 66044. Received October 23, 1969

Abstract: Nmr and uv spectral data are presented to show that two 1:1 covalent adducts are formed by addition of bisulfite ion to 2-amino-1-methylpyrimidinium ion (I) in water. One of these products is shown from its X-ray diffraction pattern to be 2-amino-1,6-dihydro-1-methylpyrimidinium-6-sulfonate (II) and the other is believed to be 2-amino-3,4-dihydro-1-methylpyrimidinium-4-sulfonate (III). In dilute aqueous solutions at 32° the initial reaction yielded a 1.3:1 ratio of the products II and III. However, this was a kinetically controlled "pseudo-equilibrium" and a subsequent slow interconversion of isomers yielded an equilibrium mixture containing a 0.8:1 mixture of the isomers II and III. An interesting feature of this system was that only isomer II could be crystallized out of concentrated aqueous solutions of the bisulfite adducts or obtained as a solid following flash evaporation of an equilibrium mixture at 25°.

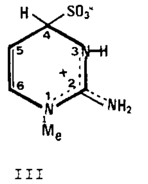
Covalent addition of bisulfite ion across cyclic imino groups (>C=N–) in nitrogen-containing heteroaromatics is now a well-recognized reaction. For example, covalent bisulfite adducts of pyridines,[2] pyrimidines,[3] pteridines,[4] and quinazolines[5] have been characterized and quantitative data on some of these systems[3,4d] have been reported. The present article deals with the structures and yields of products formed by covalent addition of bisulfite ion to 2-amino-1-methylpyrimidinium ion (I). This compound was known[3] to add bisulfite ion reversibly in aqueous



I



II



III

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[1] To whom all correspondence should be addressed.

[2] N. O. Kaplan, *Enzymes*, **3**, 105 (1960).

[3] D. D. Perrin and I. H. Pitman, *J. Chem. Soc.*, 7071 (1965).

[4] (a) M. Viscontini and H. R. Werlenmann, *Helv. Chim. Acta*, **42**, 1854 (1959); (b) C. Van Boalen and H. S. Forrest, *J. Amer. Chem. Soc.*, **81**, 1770 (1959); (c) A. Albert and F. Reich, *J. Chem. Soc.*, 127 (1961); (d) D. J. Vonderschmitt, K. S. Vitols, F. M. Hunnekens, and K. G. Scrimgeour, *Arch. Biochem. Biophys.*, **122**, 488 (1967).

[5] A. Albert, W. L. F. Armarego, and E. Spinner, *J. Chem. Soc.*, 2689 (1961).

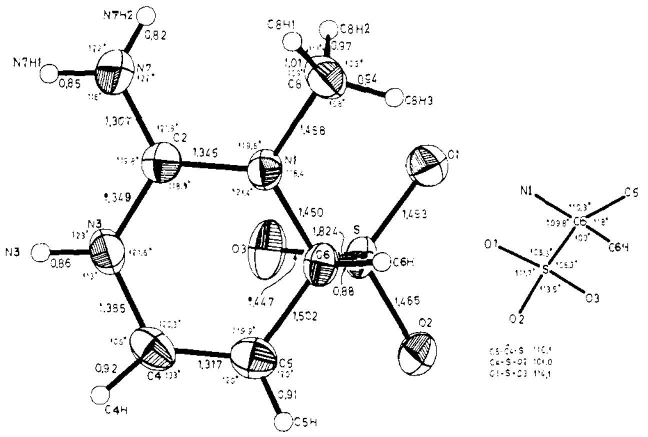

Figure 1. Molecule II as viewed perpendicular to the ring showing the various intramolecular bonding parameters. The 50% probability thermal ellipsoids are shown for the nonhydrogen atoms.

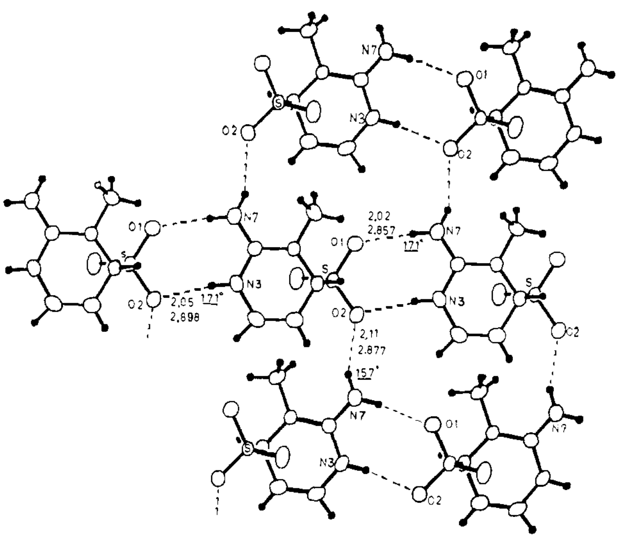

Figure 2. The hydrogen bonding scheme in the crystal, as observed in a direction perpendicular to the pyrimidine rings.

solution but it was not known whether the product was 2-amino-1,6-dihydro-1-methylpyrimidinium-6-sulfonate (II) or 2-amino-3,4-dihydro-1-methylpyrimidinium-4-sulfonate (III), or a mixture of both.

Structure of the Crystalline Adduct

When equal volumes of deuterium oxide solutions of the chloride of I (2.7×10^{-1} *M*) and sodium bisulfite (4.8×10^{-1} *M*) were mixed and left to stand at 25° for 24 hr, colorless crystalline plates formed. This material had the elemental analysis of a 1:1 adduct of I and bisulfite ion and its ultraviolet spectrum (λ_{max} 258 mμ, log ϵ 3.38) in aqueous sodium bisulfite solution (2×10^{-2} *M*) was similar to that of other covalent adducts of pyrimidinium ions.[3] Single-crystal X-ray analysis of this material showed it to be the isomer II. There did not appear to be any of isomer III present in the crystalline material.

A view of the molecule showing all the intramolecular bonding parameters is shown in Figure 1. The esd (estimated standard deviations) of the bond lengths and angles were on the average 0.006 Å and 0.2°, with the exception of those involving hydrogens which were approximately ten times as great.

The sulfonate portion of the molecule was slightly distorted from tetrahedral symmetry, in a manner not untypical of that found in SO_3^- structures.[6] The differences in the S–O bond lengths seem to influence or be influenced by the hydrogen bonding within the crystal. The longer the S–O bond the greater the basic character of the oxygen and thus the more susceptible it should be to hydrogen bonding. O(2) participated in two such intermolecular interactions while O(1) was involved in only one link and O(3) in none. The Π-bond order of each S–O bond was approximately 0.6 ± 0.05, estimated using Cruickshank's parameters.[7] The average S–O length (1.455 Å) agreed quite well with the value of 1.45 Å presented by Hall and Maslen[6] for orthanilic acid. The carbon-to-sulfur bond of 1.82 Å was in excellent agreement with the C–S single bond length calculated by Trinajstić.[8]

The molecule existed in the zwitterionic form with the sulfonic acid proton on N(3). A consideration of the bond orders in the N(3)–C(2)–N(3) portion of the molecule suggested that the charge was delocalized over this portion of the molecule. The near equivalency of the hydrogen bond lengths in this structure (see Figure 2) is somewhat suggestive that the acidic character of the N(7) and N(3) protons is approximately equivalent. These lengths are all reasonably close to the average N–H···O$^-$ distance of 2.84 Å given by Wallwork.[9]

As would be expected, the addition of bisulfite led to a substantial degree of puckering of the heterocyclic ring. The N(3), C(2), N(1), and N(7) atoms were coplanar within experimental error. However, C(8) was significantly displaced (by 0.18 Å) out of the plane through these four atoms (see Table I). The displacement was to the opposite side of the SO_3^- group and probably resulted from nonbonded repulsive forces between the two molecular entities. The puckering of the ring is clearly evident from the least-squares planes shown in Table I.

Table I. Deviations from Some Least-Squares Planes

Atoms comprising plane	Displacement, Å	Other atoms	Displacement, Å
N(1)	0.001	C(4)	0.180
C(2)	−0.003	C(5)	0.044
N(3)	0.001	C(6)	−0.353
N(7)	0.001	C(8)	0.179
		N(3)H	0.13
		N(7)H(1)	0.14
		N(7)H(2)	−0.11
$0.3646X + 0.2149Y + 0.9309Z - 5.7653$ Å $= 0$			
N(1)	0.022	C(6)	−0.380
C(2)	0.004	S	−2.170
N(3)	−0.053	N(7)	0.054
C(4)	0.076	C(8)	0.265
C(5)	−0.049	C(6)	−0.380
		C(6)H	0.265
$0.3598X - 0.02607Y + 0.9327Z - 5.6077$ Å $= 0$			

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(6) S. R. Hall and E. N. Maslen, *Acta Crystallogr.*, 22, 216 (1967).
(7) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).
(8) N. Trinajstić, *Tetrahedron Lett.*, 12, 1529 (1968).
(9) S. C. Wallwork, *Acta Crystallogr.*, **15**, 758 (1962).

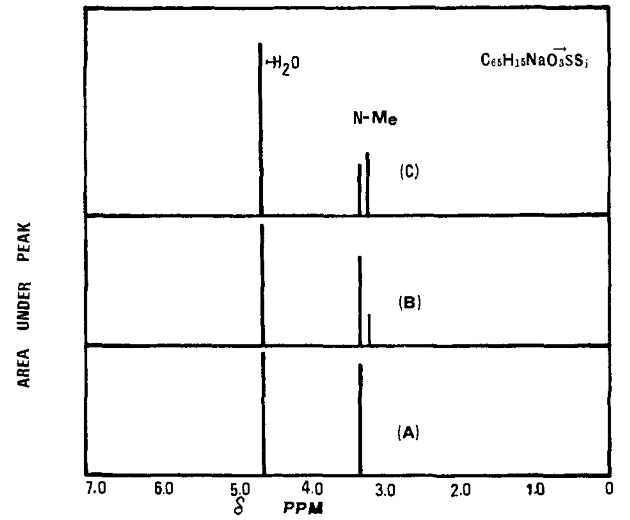


Figure 3. Nmr spectra that were measured (a) 3 min, (b) 15 min, and (c) 1 hr after a solution of II in a deuterium oxide solution of sodium bisulfite had been prepared.

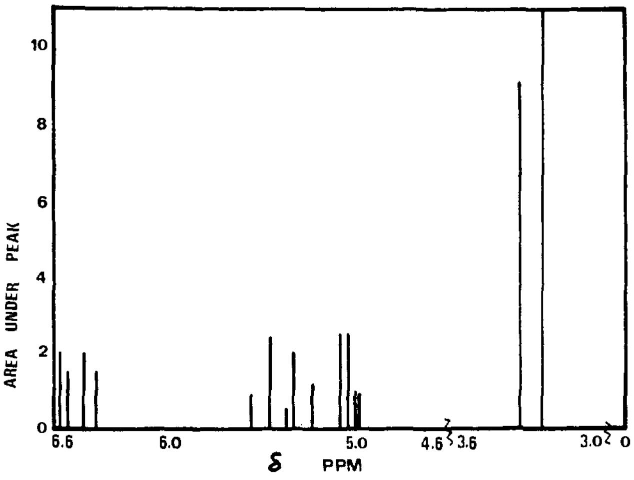
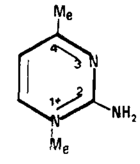


Figure 4. Nmr spectrum of the equilibrium solution obtained following the mixing of deuterium oxide solutions of sodium bisulfite (4.8 × 10^{-1} *M*) and the chloride of I (2.7 × 10^{-1} *M*) at 32°. Chemical shifts are measured downfield from the methyl resonance of 3-(trimethylsilyl)propanesulfonic acid sodium salt.

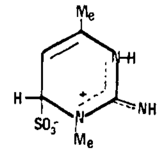
Isomerization of II to III

Figure 3 shows the nmr spectra that were measured (a) 3 min, (b) 15 min, and (c) 1 hr after a solution of crystals of II in a deuterium oxide solution of sodium bisulfite had been prepared. The singlet at δ 3.34 that was present initially is believed to be caused by resonance of the methyl protons of II (*cf.* δ 4.01 for resonance of the methyl protons of I[3]). The new singlet which slowly developed at δ 3.24 as the intensity of the singlet at δ 3.34 decreased is believed to be caused by resonance of the methyl protons of III which would be formed by isomerization of II. The failure to observe the peaks caused by resonance of the protons on C(4), C(5), and C(6) of II and III was due to the difficulty of rapidly preparing sufficiently concentrated solutions of II. The nmr spectrum of a more concentrated equilibrium solution of the adducts is shown in Figure 4 to contain, in addition to the two singlets at δ 3.34 and 3.24, two complex quartets at δ 6.45 and 5.04 and a complex series of peaks centered at δ 5.45. The ratio of the areas under the quartets at δ 6.45 and 5.05, the peaks centered at δ 5.45, and the sum of the areas under the two singlets was 1 : 1 : 1 : 3 at equilibrium. This spectrum was consistent with that which would be predicted for a solution of the two isomers II and III, each of which contained an N–CH$_3$ group and three protons linked in similar ABX systems.

Another possible explanation of the observed results would be that the isomer III was never formed but that while the structure II existed predominantly in one conformation in the crystalline state, it could adopt two distinct conformations about the C(6)–N(1)–C(8) bonds in solution. The observed changes in the nmr spectra of solutions of the crystals would thus be due to a conformational rather than a structural isomerization. This theory was discounted by comparison of the nmr spectra of the bisulfite adduct of 2-amino-1,4-dimethylpyrimidinium ion (IV) with that of the equilibrium solution shown in Figure 4. Addition to compound IV would yield predominantly 1,6-dihydro-1,4-dimethylpyrimidinium-6-sulfonate (V) because of the known[10] blocking effects of C-methyl groups (in heteroaromatic molecules) to nucleophilic additions to the carbon atom on which they are located. Thus, while addition of bisulfite ion to IV would yield only one structural isomer (and not two isomers corresponding to II and III) the adduct would be expected to take up similar conformations in solution to compound II. However, the nmr spectrum of a solution of V had only a single N–CH$_3$ resonance peak (δ 3.35), suggesting that it existed predominantly in one stable conformation about the C(6)–N(1)–C(8) system. Consequently, it is concluded that the two singlets at δ 3.34 and 3.24 in the spectrum of an equilibrated mixture of the addition products of I were caused by the N-methyl protons of the structural isomers II and III.



IV



V

The difference in free energy between the two isomers at 32° was calculated from the ratio of areas under the singlets at equilibrium and found to be 135 cal mol^{-1} with isomer III being the more stable. Between 16 and 60° III was always the more stable isomer and the difference in free energy did not appear to vary very much. In contrast to this small difference in free energy between the two isomers in solution, isomer II appeared to be considerably more stable than III in the crystalline state because it was the only one that crystallized from a saturated equilibrium solution at 25°. A surprising feature of this system was that the powder obtained when an aqueous solution of the adduct was evaporated under reduced pressure at 25° also appeared to consist of only isomer II because when it was redissolved in deuterium oxide and its nmr spectrum measured, only the singlet at δ 3.34 was observed initially.[11] The apparent differences in the

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[10] A. Albert and W. L. F. Armarego, *Advan. Heterocycl. Chem.*, **4**, 1 (1965).

[11] It seems likely that a solid mixture of the two isomers was obtained following rapid freezing and lyophylization of a reaction mixture

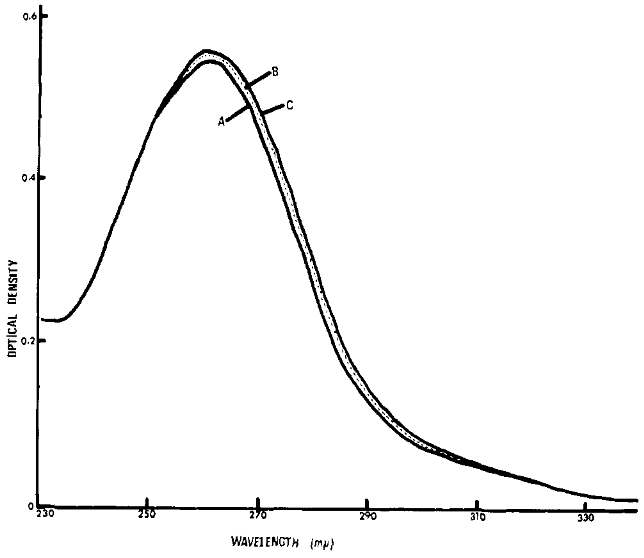

Figure 5. Ultraviolet spectra of a solution of the crystalline adduct (2.45×10^{-4} *M*) in aqueous sodium bisulfite (5×10^{-2} *M*): (A) 6 min after mixing, (B) 14 min after mixing, (C) 20 min after mixing.

stability of the crystals of the two isomers are believed to arise, in part, from differences in the number of intermolecular hydrogen bonds which each can form with neighboring molecules. Thus, whereas the proton on N(3) in isomer II forms a hydrogen bond with an oxygen atom of a neighboring molecule (Figure 2), the same proton in isomer III is likely to form an intramolecular hydrogen bond with a sulfite oxygen atom on C(4).

The isomers II and III appeared to have slightly different ultraviolet spectra in water and the slow interconversion of isomers could be followed by changes in ultraviolet absorption. Figure 5 shows the ultraviolet spectrum of a solution of the crystalline adduct (2.45×10^{-4} *M*) in aqueous sodium bisulfite (5×10^{-2} *M*) (a) 6 min after mixing, (b) 14 min after mixing, and (c) 20 min after mixing. The spectral changes suggest that the isomer III has a λ_{max} value at slightly higher wavelength than the isomer II and that its extinction coefficients are higher between 255 and 305 mμ. The previously reported[2] λ_{max} and extinction coefficient for the covalent bisulfite adduct of I obviously apply to an equilibrium mixture of the two isomers.

Relative Rates of Formation of Isomers in Dilute Solution

The two singlets at δ 3.34 and 3.24 due to the methyl protons of the two isomers were present in the nmr spectrum of a solution obtained 3 min after mixing deuterium oxide solutions of the chloride of I (1.35×10^{-1} *M*) and sodium bisulfite (2.4×10^{-1} *M*). This spectrum contained no singlet at δ 4.01 due to the methyl protons in I[3] thus indicating that after 3 min the covalent addition reaction was virtually complete. This assumption was consistent with the independently measured kinetics of the addition reaction.[12] While the nmr spectrum showed that both isomers had been formed within 3 min it showed that the ratio of areas under the two peaks was different from that pertaining at equilibrium. After 3 min the ratio of isomers was 1.3:1 with the isomer II predominating. Over a period of 20 min the nmr spectrum changed to yield the previously measured ratio of 0.80:1 with the isomer III predominating. Thus it appears that II was formed slightly more rapidly than III in aqueous solution to yield a pseudoequilibrium system, but that a subsequent slower interconversion of isomers eventually yielded the thermodynamic equilibrium mixture. The changes in ultraviolet absorbance which followed mixing of aqueous solutions of the chloride of I and sodium bisulfite were consistent with this hypothesis. Thus, after all of I had been consumed, a small increase in absorbance occurred between 255 and 305 mμ due to the formation of more of III by the isomerization of II.

These results shed some light on the relative reactivity toward nucleophiles of the $>C(6){=}N(1)^{+}<$ and $>C(4){=}N(3)-$ imino groups in N(1) alkylated pyrimidinium ions. This knowledge is particularly important when postulating the addition of nucleophiles to either of these sites as being the first step in a reaction sequence. For example, while the addition of hydroxide ion to C(6) of I has been postulated[2] to be the reaction which precedes fission of the $>C(6){=}N(1)^{+}<$ bond and allows a Dimroth rearrangement to occur, it is likely that addition also occurs at C(4).

Experimental Section

Nmr spectra were obtained from Varian HR-100 and Varian A-60-A spectrometers. Ultraviolet spectra were run on a Cary 14 spectrophotometer. All X-ray measurements were carried out on a General Electric XRD-6 diffractometer equipped with a single-crystal orientor.

2-Amino-1,6-dihydro-1-methylpyrimidinium-6-sulfonate (II). This compound was crystallized as described in the text from both aqueous and deuterium oxide solutions. The sample crystallized from water had, after washing and drying over $CaCl_2$, the elemental analysis of the 1:1 bisulfite adduct. *Anal.* Calcd: C, 27.12; H, 3.98; N, 23.72; S, 18.10. Found: C, 26.98; H, 4.12; N, 23.30; S, 18.33.

2-Amino-1,6-dihydro-1,4-dimethylpyrimidinium-6-sulfonate (V). This compound was prepared *in situ* by mixing 2 ml each of deuterium oxide solutions of 2-amino-1,4-dimethylpyrimidinium iodide[13] (IV) (0.05 g) and sodium bisulfite (0.38 g) and allowing the mixture to stand for 15 min. The fact that the covalent addition of bisulfite had occurred was deduced from differences between the nmr spectra of this solution and that of a deuterium oxide solution of IV. The solution of IV had doublets at δ 8.20 (4 H) and 7.70 (5 H) (one proton each, $J = 7.0$ cps) and singlets at 3.82 (N-Me) and 2.56 (C-Me) (3 protons each) while that of the adduct had a complex series of peaks centered at δ 5.01 (1 proton) and singlets at δ 3.31 (N-Me) and 1.90 (C-Me) (3 protons each).

X-Ray Studies. The following crystallographic data were measured for the colorless monoclinic platelets of II: $a = 7.235$ (0.001) Å; $b = 11.809$ (0.002) Å; $c = 10.228$ (0.001) Å; $\beta = 118.69$ (0.01)°, *D*[measured] = 1.66 g/cm³; *D*[calcd] = 1.674 g/cm³; $Z = 4$; space group, $P2_1/c$.

A fragment of one of the plates measuring $0.4 \times 0.1 \times 0.2$ mm was utilized for the intensity data collecton. These data were measured by the stationary-counter-stationary-crystal technique[14] using balanced filters for the Cu Kα radiation (Ni *vs.* Co). There were 1144 independent reflections within the 2θ range of 0-120° and of these, 1095 had peak counts which were significantly greater than their respective backgrounds. The transmission factor as a function of φ at χ equal to 90° was measured for the 040 reflection and utilized as an approximate correction for absorption (correction

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which had equilibrated at 25°. Thus, the nmr spectrum of a solution obtained 3 min after dissolving this solid material in deuterium oxide had nmr peaks at δ 3.34 and 3.24.

[12] I. H. Pitman and M. Ziser, unpublished results.

[13] D. J. Brown and M. N. Paddon-Row, *J. Chem. Soc., C*, 1928 (1967).

[14] T. F. Furnas and D. Harker, *Rev. Sci. Instrum.*, **26**, 449 (1955).

Table II. Positional and Thermal Parameters[a]

Atom	x/a	y/b	z/c	b_{11}/B_{iso}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S	7974 (1)	2870 (1)	2197 (1)	94 (2)	43 (1)	68 (1)	8 (2)	11 (3)	6 (1)
O(1)	7011 (2)	1790 (2)	2194 (3)	143 (6)	43 (2)	119 (4)	−21 (6)	135 (9)	−17 (5)
O(2)	6774 (4)	3822 (2)	2327 (3)	147 (7)	48 (2)	127 (4)	32 (6)	170 (9)	19 (5)
O(3)	8486 (5)	2999 (3)	1001 (3)	163 (8)	89 (3)	66 (4)	3 (7)	128 (9)	9 (5)
N(3)	13649 (5)	3150 (3)	3179 (4)	144 (9)	48 (3)	106 (5)	−6 (7)	151 (11)	27 (6)
C(2)	13146 (6)	2097 (3)	3416 (4)	94 (9)	41 (3)	62 (5)	10 (8)	44 (11)	4 (6)
N(1)	11801 (5)	1989 (3)	3967 (4)	124 (8)	40 (2)	70 (4)	19 (7)	108 (10)	22 (5)
C(6)	10468 (6)	2918 (3)	3927 (4)	134 (10)	47 (3)	55 (5)	4 (9)	101 (11)	4 (6)
C(5)	11552 (6)	4029 (3)	4054 (4)	157 (10)	43 (3)	76 (5)	−21 (9)	73 (12)	−13 (6)
C(4)	13035 (6)	4102 (3)	3662 (4)	136 (10)	43 (3)	82 (5)	−35 (9)	55 (12)	13 (7)
N(7)	13980 (5)	1219 (3)	3121 (4)	167 (9)	52 (3)	136 (6)	−12 (8)	197 (13)	20 (6)
C(8)	11447 (7)	876 (3)	4423 (5)	179 (11)	43 (3)	100 (6)	−23 (10)	141 (13)	18 (7)
N(3)H	14651 (67)	3281 (38)	2973 (47)	3.2 (0.9) Å^2					
N(7)H(1)	14975 (66)	1352 (36)	2932 (42)	2.9 (0.9)					
N(7)H(2)	13587 (74)	573 (41)	3136 (52)	4.2 (1.1)					
C(6)H	10016 (64)	2773 (33)	4571 (46)	2.4 (0.9)					
C(5)H	11201 (60)	4651 (34)	4416 (42)	2.3 (0.8)					
C(8)H(1)	12849 (98)	517 (53)	5097 (71)	7.3 (1.6)					
C(8)H(2)	10633 (76)	411 (43)	3556 (55)	4.2 (1.1)					
C(8)H(3)	10599 (86)	968 (48)	4884 (63)	5.7 (1.3)					
C(4)H	13845 (66)	4688 (36)	3632 (48)	2.9 (0.9)					

[a] With their corresponding standard deviations in parenthesis (× 10^4). Thermal parameters defined by $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

varied by ±17%). The usual Lorentz polarization factors as well as a correction for the α_1–α_2 splitting were applied to the data.[15] The structure factor amplitudes, $|F|_o$'s, were put on an absolute scale by the use of Wilson statistics[16] and then converted to their corresponding normalized structure factors, $|E|$'s.

Application of the Sayre relationship[17] to 152 reflections having $|E|$'s greater than 1.5 enabled their respective phases to be derived. The method is well described in the literature[18] and will not be dealt with here. A program written by R. Long was utilized for these calculations.[19] The E map (Fourier synthesis whose coefficients are the normalized structure factors) computed with the most consistent set of phases permitted all the nonhydrogen atoms of the molecule to be located.

The positional and thermal parameters of the molecule were subsequently refined by least squares using a block diagonal approximation. Hydrogen atoms were easily located in a difference electron density map after the R value had reached 0.08. These were included in the final cycles of least squares. In the last stages of refinement the weighting scheme was chosen such that $\langle w\Delta^2\rangle$ was constant over the whole range of $|F_o|$'s, *i.e.* $w^{-1} = 4.77 - 0.94\,|F_o| \pm 0.06\,|F_o|^2$. The function minimized is $\Sigma w(F_o - F_c)^2$. The unobserved data were given zero weight throughout the refinement. The final R value was 0.057 for all the data. The parameters obtained at the conclusion of the least-squares refinement are listed in Table II together with their respective esd. A list of the observed and calculated structure factors can be obtained from the authors on request.

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