Infrared and Mass Spectra of Purine and Substituted Dihydropurines (1)

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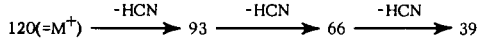
Infrared spectra (potassium bromide) of purine, 7(9)-deuteriopurine, 6-deuteriopurine, 8-deuteriopurine and a number of substituted dihydropurines are presented. The latter compounds are the 6-α-hydroxyalkyl-1,6(or 3,6)dihydropurines formed by photoaddition of the respective alcohols to purine (4-6). From the comparative spectra of purine and its monodeuterated derivatives, it is possible to make assignments of N-H and N-D stretching vibrations and tentative assignments of C-H deformation modes. The spectra of the substituted dihydropurines show evidence of interesting hydrogen-bonding interactions which are demonstrated most clearly in the distinct differences between the spectra of the diastereomeric purine-ethanol adducts. Mass spectra of these compounds all indicate progressive scission of HCN molecules from the principal radical-ion. In the case of the photo-adducts, HCN scission is preceded by scission at the site (*i.e.* 6-position) of alcohol addition to the purine ring.

Introduction.

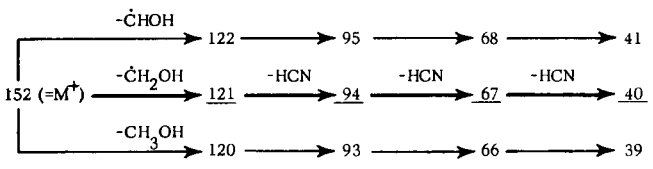
Ultraviolet (2537 Å) irradiation of unsubstituted purine (I) in deoxygenated alcohol solutions results in efficient ($\Phi_{2537} \sim 0.23$) addition of α-hydroxyalkyl groups to the 6-position of the purine ring (4-6). The structural proofs of the adducts (Figure 1), within the ambiguity of the four tautomeric structures possible in each case, have been presented elsewhere (4-6). The infrared and mass spectra of these new compounds are presented here in the belief that these data will be of some relevance to future work on this potentially important new class of compounds.

Mass Spectra.

The fragmentation patterns of the purine-alcohol adducts observed at an ionization energy of 70 eV (Figures 2-4) correspond to scission at the site of photochemical addition to yield radical-ions of purine and radicals of the respective alcohols, followed by successive elimination of HCN units from the purine radical-ion. This pattern of sequential HCN loss is characteristic of purine itself (7, and Figure 2a), as well as substituted purines (8) and pyrimidines (9), indicating retention of the heterocyclic skeleton in the photoadducts. In the purine spectrum, conclusive evidence for the progressive scission of HCN in the sequence (numbers indicate prominent m/e peaks):

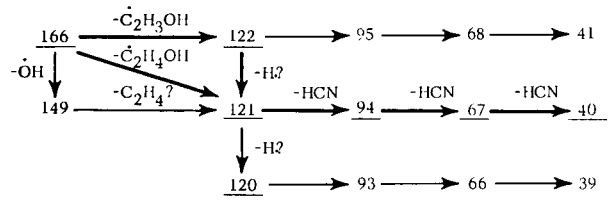


is provided by the appearance of metastable peaks at m/e 72.1(72.14), 46.9(46.88), and 23.1(23.07). The values in parentheses are predicted (10) by the relation $M^* \sim (M - x)^2/M$, and where M* is the m/e value of the metastable peak resulting from scission, in the field-free region of the spectrometer, of a neutral fragment of mass x from an ion of m/e = M. Similarly in the mass spectrum of the purine-methanol adduct, II, (Figure 2b), there are prominent metastable peaks (not shown in the Figure) at m/e 96.3(96.26), 73.1(73.10), 47.7(47.81), and 23.8(23.91), with weaker metastable peaks very close to one m/e unit on either side of each prominent metastable peak. These observations are consistent with fragmentation *via* the following pathways:



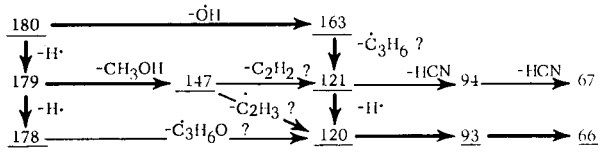
The heavy arrows indicate the apparently predominant pathway and the underlined numbers are the most intense m/e peaks.

The fragmentation patterns of the ethanol adducts, III and IV, (Figure 3) are virtually identical, which proves that the compounds are isomers, although a choice between stereo-isomers and positional isomers cannot be made on the basis of this evidence alone (11). The prominent peaks at m/e 166, 121, 94, 67, and 40 suggest that the predominant fragmentation pathway is analogous to that of adduct II, and indeed prominent metastable peaks are observed at m/e 73.1(73.10), 47.7(47.81), and 23.9(23.91) together with much weaker metastable peaks approximately one m/e unit on either side. However, for scission of a C_2H_4OH radical (mass 45.06) from the parent radical ion, M^+ (m/e 166), a metastable peak is predicted at m/e 88.28. Although a very weak metastable peak is observed at this value, the dominant metastable peak in this region is at m/e 89.7, which is in good agreement with the calculated value (m/e 89.76) for: 166 $\xrightarrow{-\dot{C}_2H_3OH}$ 122. The importance of such a process is also suggested by the ratio of peak heights at m/e 122 and 121, which is considerably higher than the value of 7% predicted solely on the basis of the natural isotopic abundances of N^{15} and C^{13} (12). A peak of moderate intensity is observed at m/e 149, and this is apparently due to loss of $\dot{O}H$ (mass 17) from the parent radical-ion, although no metastable peak for this process was observed at the predicted m/e 133.91. There is a very weak metastable peak at about m/e 98 (*vs.* 98.34, calcd.) corresponding to the process 149 $\xrightarrow{-C_2H_4}$ 121. For the process 122 $\xrightarrow{-H\cdot}$ 121, a metastable peak is predicted at m/e 120, which if present is obscured by the relatively intense purine radical-ion peak at this same value. It should be born in mind that the absence of a metastable peak at the m/e value predicted for a given process does not prove that the process does not occur (8). Thus the fragmentation pattern of the ethanol adducts is consistent with the pathways:



Again, the heavy arrows represent the suggested predominant fragmentation pathways and the underlined numbers the most intense m/e peaks.

The mass spectrum of the purine-2-propanol adduct, V, is also somewhat more complicated than might be expected by analogy to that of adduct II. Thus, in Figure 4, the principal peak is at m/e 120 rather than at 121 as observed in the fragmentation patterns of the other adducts. Furthermore, the parent peak of V (m/e 180) is much weaker, relative to the principal peak, than are the parent peaks of the other adducts. This may be attributed to the importance of processes involving loss of two H atoms (or an H_2 molecule) to give m/e 178, loss of an H atom (8,9) followed by loss of CH_3OH to give m/e 147, scission of an OH group to give m/e 163, and possibly loss of either C_2H_4OH or C_2H_5OH to give peaks at m/e 135 and 134, respectively. Comparison of the spectra of all four adducts suggests that such processes are more important in the fragmentation of V than in the other cases. The spectrum of V shows weak metastable peaks at m/e 98.3 (147 $\xrightarrow{-\dot{C}_2H_3}$ 120, $M^*_{calcd.}$ = 97.94), m/e~90 (163 $\xrightarrow{-\dot{C}_3H_6}$ 121, $M^*_{calcd.}$ = 89.89), m/e 72.1 and 46.8 (120 $\xrightarrow{-HCN}$ 93 $\xrightarrow{-HCN}$ 66), and very weak metastable peaks at m/e~73 and ~48 (121 $\xrightarrow{-HCN}$ 94 $\xrightarrow{-HCN}$ 67). The predominant fragmentation processes suggested by the mass spectrum of adduct V are as follows:



Obviously, detailed mechanism of fragmentation under electron impact must await high-resolution studies at various ionization energies on isotopically substituted adducts, similar to the definitive study of Tatematsu, *et al.* (7) on purine itself. The most important conclusions to be drawn from the results of the mass spectrometric studies of the adducts are the exact correspondence of the molecular weights (*i.e.*, the m/e values of the parent peaks) to the values calculated for 1:1 addition of each alcohol to purine; the retention of the purine ring in the structures of the adducts; and the isomeric nature of the two ethanol adducts.

Infrared Spectra.

Beginning with the pioneering work of Blout and Fields (13) in the early 1950's, a great deal of attention has been focused on the ir spectra of purines and pyrimidines. Most studies, however, have dealt with compounds of biological interest and have been concerned with structural aspects such as lactam-lactim tautomerization (13-16) or

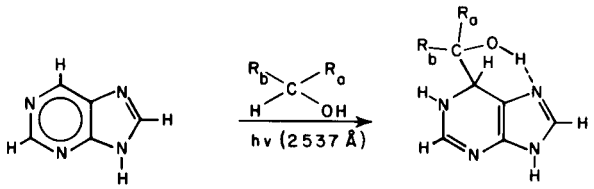


Figure 1. Suggested structure of purine-alcohol adducts (1,9-tautomeric form) shown in the conformation, inferred from nmr spectra (4-6), resulting from strong *intra*molecular O-H···N_7 hydrogen-bonding. Letter designations are: II (methanol adduct; R_a = R_b = H); III (ethanol adduct; R_a = Me, R_b = H); IV (ethanol adduct; R_a = H, R_b = Me); and V (2-propanol adduct; R_a = R_b = Me). These designations are consistent with those used previously (4-6). Other tautomeric and hydrogen-bonded structures are possible (see text).

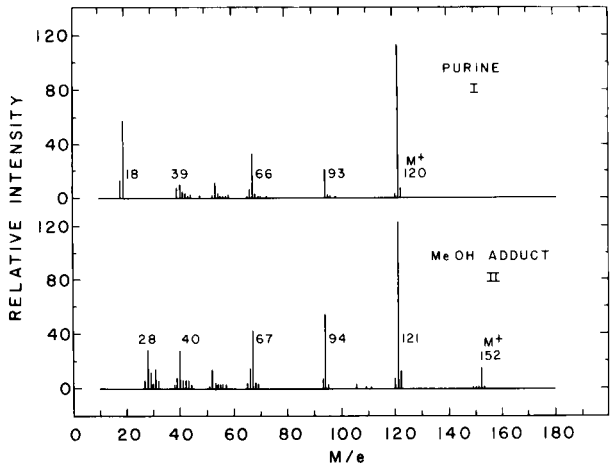


Figure 2. Mass spectra of purine (upper) and purine-methanol adduct, II, (lower). Ionization energy = 70 eV; ion chamber temperatures 210° (purine) and 195° (II). Metastable peaks at m/e 72.1, 46.8, and 23.1 (purine) and at m/e 96.3, 73.1, 47.7 and 23.8 (II) not shown (see text).

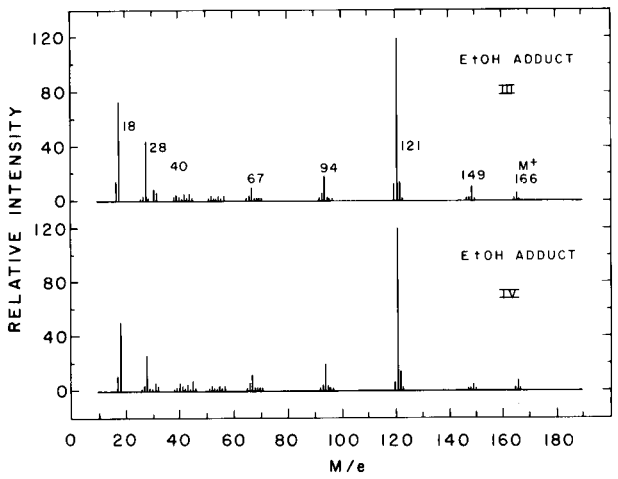


Figure 3. Mass spectra of isomeric ethanol adducts of purine, III (upper) and IV (lower). Ionization energy = 70 eV; ion chamber temperatures 195° (III) and 200° (IV). Metastable peaks at m/e 89.7, 73.1, 47.7 and 23.8 not shown (see text).

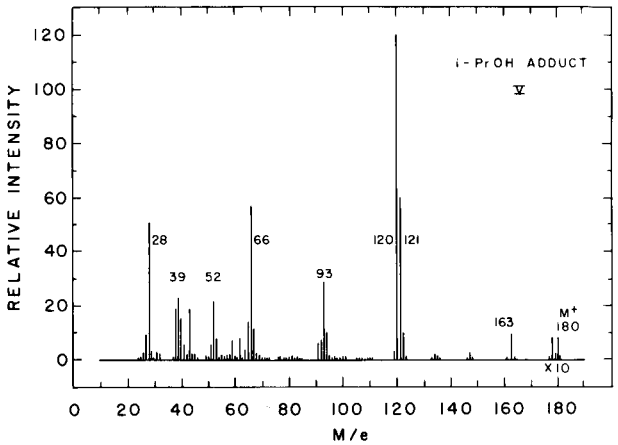


Figure 4. Mass spectrum of purine-2-propanol adduct, V. Ionization energy = 70 eV; ion chamber temperature 170°. Metastable peaks at m/e 98.3, ~90, 72.1 and 46.8 not shown (see text).

specific hydrogen-bonding interactions of nucleic acid constituents (17).

Not surprisingly, ir spectra of purines are very complex (Figure 5) and specific assignments of bands are difficult. Studies of *inter*- and *intra*molecular H-bonding are hampered by the limited solubilities of these compounds in the solvents commonly used in ir spectroscopy. Thus, previous spectra have been taken on evaporated or sublimed films (13,14), Nujol mulls (15), or molten antimony trichloride (16).

Only two previous studies of the ir spectra of unsubstituted purine appear to be available in the literature. Willits, *et al.* (14) compared the spectra of sublimed films of a number of purines with the spectra of related pyrimidine and quinazoline structures. On this basis, they assigned two strong bands in the 1620-1550 cm^{-1} region to C=C and C=N vibrations of the purine ring. In the case of unsubstituted purine, they noted an extremely broad band in the 3500 to 2500 cm^{-1} region, which they assigned to an exceptionally strong *inter*molecular hydrogen-bond involving the H-atom attached to the 7(9)-nitrogen. This assignment was later confirmed by the independent,

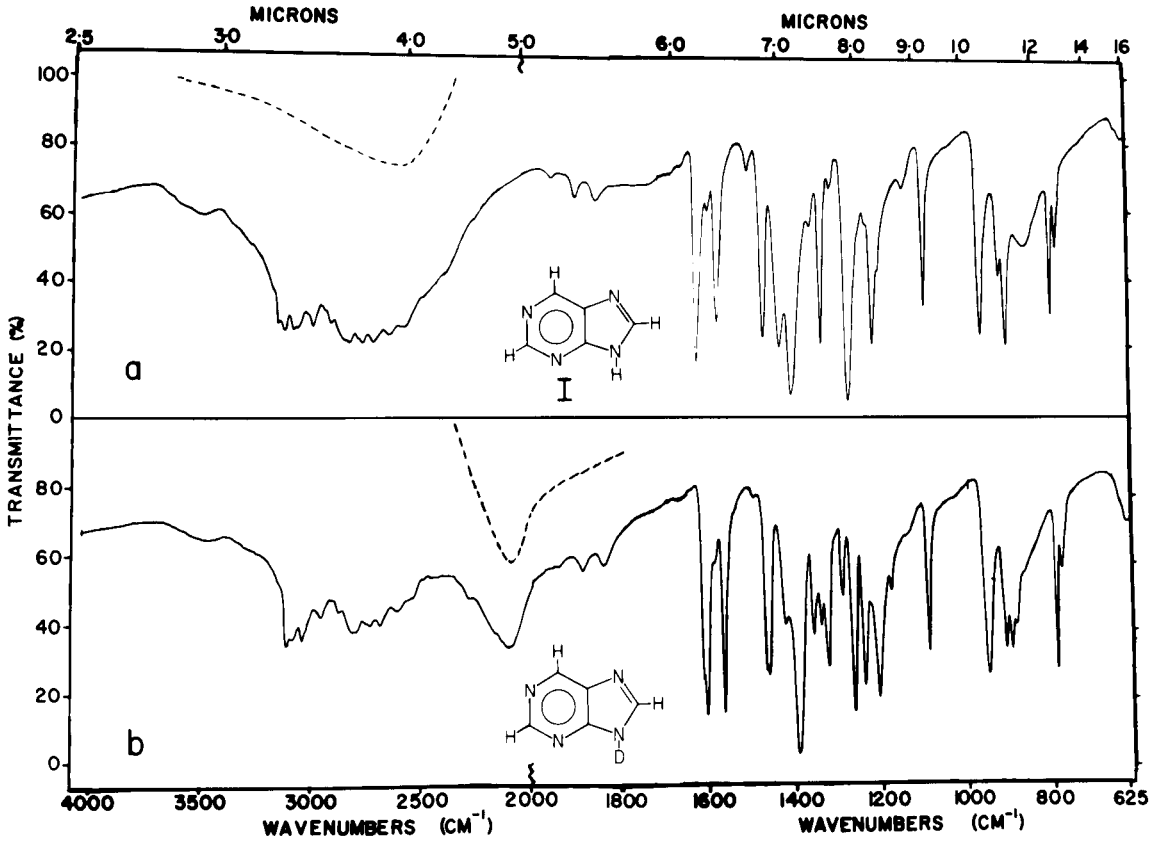


Figure 5. Ir spectra of purine (upper) and 7(9)-deuteriopurine (lower), each ~0.5 wt% in potassium bromide. Dashed lines are difference spectra representing the N-H (upper) and N-D (lower) stretching vibrations, and were obtained, respectively by subtracting spectrum (b) from (a) in the 3500-2300 cm^{-1} region and (a) from (b) in the 2300-1800 cm^{-1} region, making appropriate base line corrections.

but jointly published, crystallographic studies of Watson, and Sweet and Marsh (18). The existence of strong *inter*molecular H-bonds was also inferred by Brown and Mason (19) on the basis of their observation that the N-H stretching frequency is shifted from 3441 cm^{-1} in dilute chloroform solution (concentration and cell path not specified) to 2724 cm^{-1} in potassium bromide preparations. The assignment of this band to an N-H stretching mode was confirmed by deuterium substitution, the corresponding N-D band appearing at 2095 cm^{-1} in potassium bromide. Assignments of the remaining 25-odd bands were not attempted.

Ir spectra of a wide variety of *N*-heterocyclic molecules have been reviewed extensively by Katritzky and Ambler (20) and the general features of the spectra of purines, pyrimidines and related compounds are discussed in a number of sources (21,22).

Figure 5 shows ir spectra (potassium bromide) of comparable concentrations (*i.e.*, ~0.5 wt.%) of purine and 7(9)-deuteriopurine. The general features of these spectra coincide with previously published spectra (14,19). The dotted lines in the figure represent the difference spectra in the relevant spectral regions, and hence show the approximate band shapes of the N-H (Figure 5a) and N-D (Figure 5b) stretching vibrations. The maxima, 2650 cm^{-1} for N-H and 2100 cm^{-1} for N-D, agree fairly well with the results of Brown and Mason (see above). The narrower N-D band indicates that the *inter*molecular D-bonds are weaker than the corresponding H-bonds (21,23,24). This is consistent with the observation that in most crystalline solids, D-bonds are longer than corresponding H-bonds (25a,26).

Other isotope effects shown in Figure 5 are new bands at 1247 and 638 cm^{-1} which appear to correspond to the absence or diminution of bands at 1427 and 862 cm^{-1}, respectively. On the basis of band width and frequency, it seems reasonable to assign the broad, low frequency bands to N-H (862 cm^{-1}) and N-D (638 cm^{-1}) out-of-plane torsional modes arising from strong *inter*molecular hydrogen bonds (25b). The ν_H/ν_D ratio (1.35) is consistent with

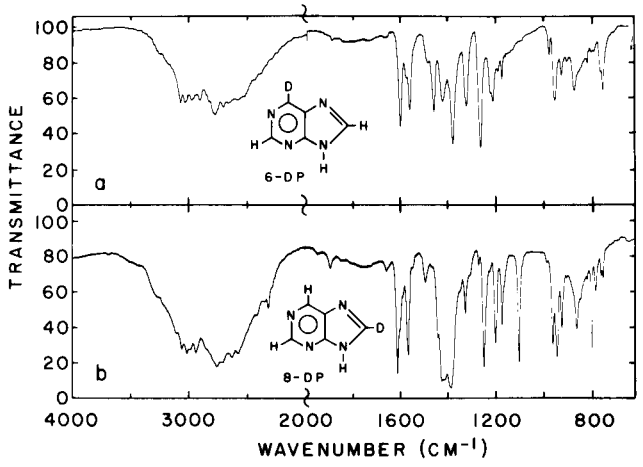


Figure 6 (a). Ir spectrum of 6-deuteriopurine (6-DP), ~0.5 wt% in potassium bromide. Purine bands at 1100, 910, and 800 cm^{-1} are missing, while new bands appear at 1170, 950, 870 and 750 cm^{-1} (compare Figures 5 and 6(b). Figure 6 (b). Ir spectrum of 8-deuteriopurine (8-DP), ~0.5 wt% in potassium bromide. Purine bands at 1270, 1210 and 910 cm^{-1} are missing, while new bands appear at 1170, 945, 860 and 760 cm^{-1} (compare Figures 5 and 6a).

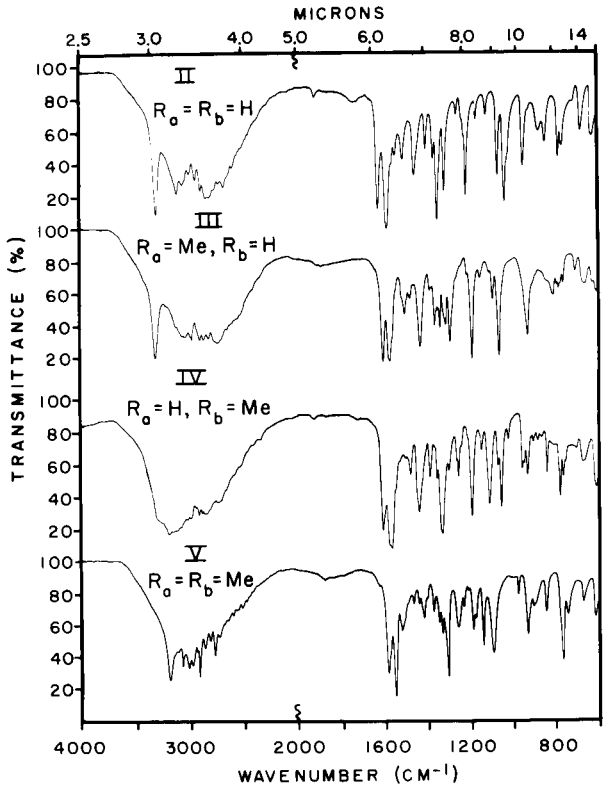


Figure 7. Ir spectra of purine-alcohol photoadducts II-V, each ~0.5 wt% in potassium bromide. Letter designations correspond to those used throughout the text.

this interpretation and is in good agreement with the comparable ratio of the stretching modes (*i.e.*, 1.26). Furthermore, the 862 cm^{-1} band is absent from the spectra of 9-methylpurine and 9-methyladenine (15).

It would be tempting to assign the 1427 and 1247 cm^{-1} bands, respectively, to N-H and N-D in-plane bending modes (21). However, the narrow bandwidths and low isotope shift (1.14) are not consistent with this interpretation (25c). Indeed, for these same reasons it is more appealing to assign these bands to =C-N-H and =C-N-D modes, for which there is some precedent (25d).

The ir spectra of 6- and 8-deuteriopurine (Figure 6) shed little light on specific assignments of group frequencies. The most notable features in the spectrum of 6-deuteriopurine (6-DP) are the absence of strong, sharp bands near 1100, 910 and 800 cm^{-1} and the presence of new bands at 1170, 950, 870, and 750 cm^{-1} (compare Figure 6a with Figures 5 and 6b). Similarly in the spectrum of 8-deuteriopurine (8-DP), strong bands at 1270, 1210 and 910 cm^{-1} are missing and new bands appear at 1170, 945, 860 and 760 cm^{-1} (compare Figure 6b with Figures 5 and 6a). In neither case do the new bands appear at the frequencies expected (27) for deuterium substitution. Nevertheless, by analogy to *N*-heteroaromatic molecules (21), the 1100 and 800 cm^{-1} bands in the purine spectrum are tentatively assigned to C-H deformation modes associated with the 6-position of the purine ring. The 1270 cm^{-1} band (and perhaps the 1210 cm^{-1} band as well) is probably due to an out-of-plane deformation mode of the H-atom bonded to the 8-carbon. This same assignment has been made by Lacher *et al.* (16) to similar bands observed in the spectra (molten antimony trichloride) of adenine, guanine, hypoxanthine and xanthine but not in uric acid (2,6,8-trihydroxypurine).

To date, no previous spectra of dihydropurines have appeared in the literature. While 1,6 (or 3,6)dihydropurine itself has been prepared electrochemically (28), only ultraviolet spectra have been published. Since infrared spectrophotometry is so often used, especially in initial identification of reaction products, we present here (Figure 7) the spectra of the methanol (II), ethanol (III and IV), and 2-propanol (V) photoadducts of purine.

All spectra show prominent bands in the 3300-2700 cm^{-1}, 1620-1575 cm^{-1} and 1150-1050 cm^{-1} regions. The bands in the lowest frequency region are readily assignable to C-OH stretching modes (21) as follows: primary alcohol (II), 1042 cm^{-1}; secondary alcohols (III and IV), 1085 and 1074 cm^{-1}, respectively; and tertiary alcohol (V), 1128 cm^{-1}. Although similar absorption bands would be expected (21) for the C-OR linkages in the respective ethers resulting from alkoxyl-type addition of the alcohols to purine, this interpretation can be ruled out on the basis of both the chemical analyses and the nmr spectra (4-6).

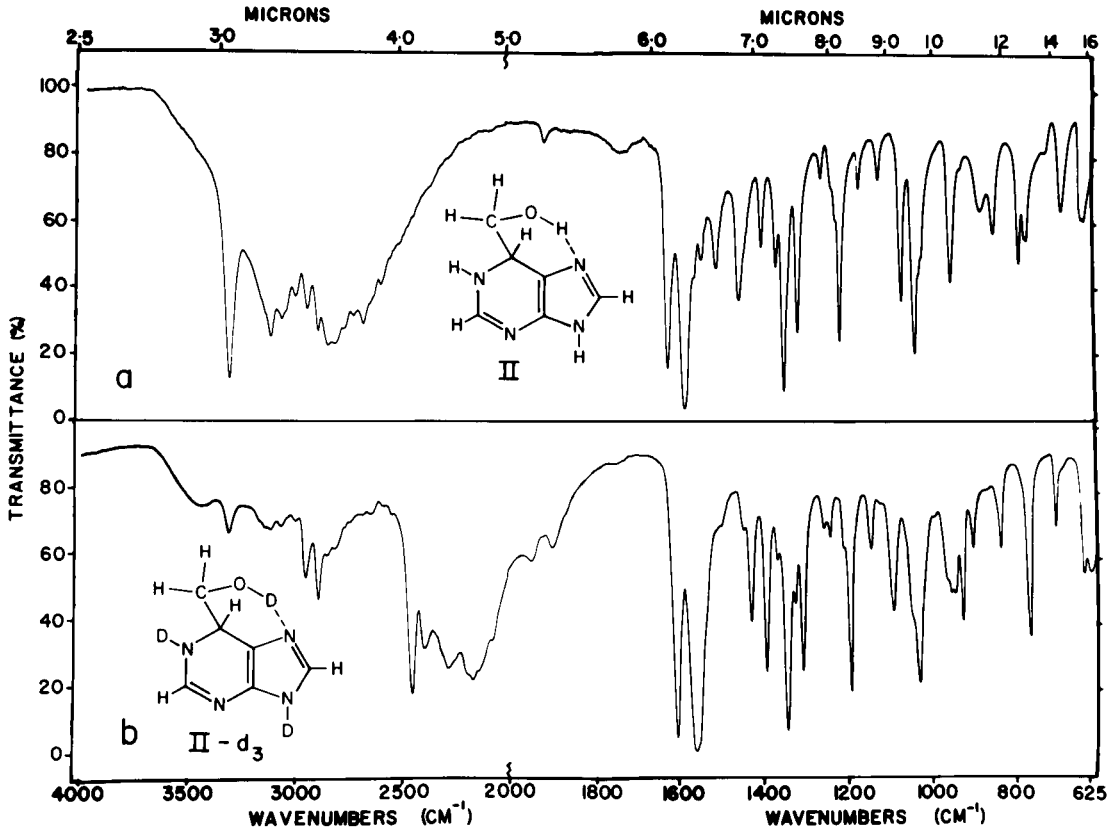


Figure 8. Comparative spectra of II (upper) and II-d_3 (lower), each ~0.5 wt% in potassium bromide. The presence of four to six new bands in the 2400-2200 cm^{-1} region of the spectrum of II-d_3 suggests that more than one tautomeric form of the adduct may exist in the solid state.

Although the uv spectra of the adducts at first suggested that alcohol addition takes place at the imidazole moiety of the purine ring to give substituted 4,5-diaminopyrimidines, we have already shown (4-6) that this possibility is inconsistent with the nmr data. The adduct ir spectra likewise exclude such an interpretation, but not nearly as conclusively. Montgomery (29) has noted the consistent appearance of five medium to strong bands in the 1670-1500 cm^{-1} region of the spectra (potassium bromide) of several substituted 4,5-diaminopyrimidines. He assigned two of these bands (1670-1650 cm^{-1}) to amine N-H bending modes and the remaining three (1585-1505 cm^{-1}) to stretching modes of the pyrimidine ring. In pyrimidine itself these ring vibrations appear at 1570 cm^{-1} (doubly degenerate) and 1467 cm^{-1} in the liquid phase (20), and at 1570, 1559, and 1466 cm^{-1} in crystalline pyrimidine (30). The only bands of comparable intensity that appear consistently in this region of the adduct spectra are strong bands at 1618 (±2) and 1580 (±5) cm^{-1} and medium to weak bands at 1450 (±5) cm^{-1}. Judging from the spectra of pyrimidine and 4,5-diaminopyrimidines, it would be difficult to assign these bands in the adduct spectra to aromatic pyrimidine ring vibrations. Although this possibility cannot be rigorously excluded, any remaining ambiguity is resolved by the definitive nmr studies (4-6).

Attempting specific band assignments in the "double bond" region of the adduct spectra is at best a hazardous procedure. Frequencies of cyclic C=C and C=N absorptions are uncertain and the effects of conjugation are usually small (21). Hence, no distinction between conjugated (*i.e.*, 1-7 and 1-9) and non-conjugated (*i.e.*, 3-7 and 3-9) tautomeric structures can be made on the basis of these ir data. However, the similarities of the adduct ir spectra, like the virtually identical chemical shifts of the ring C-H protons observed in the nmr spectra (4-6), suggest that the same C=C and C=N skeleton exists in all these adducts.

Due to the limited solubilities of the adducts in solvents such as methylene chloride, carbon tetrachloride, carbon disulfide, etc., all ir spectra were recorded on potassium bromide disc preparations. Hence interpretations of the 3300-2700 cm^{-1} region of the spectra are only tentative since it is not possible to distinguish between *inter-* and

*intra*molecular H-bonds (21). Interpretation is further obscured by the probable presence in the ir samples of "free" alcohol of crystallization (4-6). Nevertheless, the similarities of the spectra of adducts II, III and V in this region (Figure 7), are obvious, while the spectrum of IV appears to be anomalous. The differences between the spectra of the isomeric ethanol adducts (III and IV) are probably not due to alcohol of crystallization, since consistent spectra were obtained for both adducts upon recrystallization from either methanol or ethanol, followed by vacuum-drying. Before it is possible to offer an explanation for the apparently anomalous spectrum of IV in the 3300-2700 cm^{-1} region, it is necessary to attempt to understand the reasons for the general appearance of the adduct spectra in this region.

First, the band breadth is probably due to strong H-bonds. It has been established (21,24,25a) that the absorption bands due to stretching modes of H-bonded N-H and O-H groups are not only broader and more intense than absorptions of the respective free groups, but are shifted toward lower frequencies. Furthermore, these phenomena become more pronounced with increased H-bond strength. In the spectra of II and III, the overall widths of the 3300-2700 cm^{-1} bands appear to be slightly greater than those of the corresponding bands in the spectra of the other two adducts. By analogy to the spectrum of unsubstituted purine, this overall breadth is attributed to extremely strong *inter*molecular N-H···N hydrogen-bonds. Thus these interactions appear to be somewhat weaker in IV and V than in II and III. The first sharp band appears at 3280 cm^{-1} for II and III and at 3240 cm^{-1} for V, suggesting a stronger H-bond involving this group (whether N-H or O-H) in the latter case (see above). Two interpretations of this sharp band are possible, *viz.*, it may be due either to a relatively free N-H or to an *intra*molecularly hydrogen-bonded O-H stretching vibration. A free O-H stretching mode is ruled out because such vibrations usually absorb (21) at considerably higher frequencies (approximately 3600 cm^{-1}). Although stretching vibrations of *intra*molecular O-H···X hydrogen-bonds also absorb at somewhat higher frequencies (3570-3450 cm^{-1}) (21), examples of such absorptions in the 3300-3100 cm^{-1} region are well known (24). Furthermore, O-H···X *intra*molecular H-bonds are usually bent (23), and the absorption bands of the resulting stretching modes are narrower than in the case of linear *inter*molecular H-bonds. Presumably this is because the more restricted configuration in the former environment constrains the oscillators to a more harmonic potential well (23). In addition, the stretching vibrations of a wide variety of *inter*molecular O-H hydrogen bonds (both O-H···O and O-H···N types) usually absorb (24) at frequencies lower than the 3280 and 3240 cm^{-1} observed for the purine-alcohol adducts. In view of these established precedents, it appears more reasonable to assign these sharp adduct bands to *intra*molecular O-H···N hydrogen-bonds than to either free N-H or *inter*molecularly hydrogen-bonded O-H groups.

The absence of a strong, sharp peak at 3280-3240 cm^{-1} in the spectrum of adduct IV, especially as compared to the spectrum of its diastereomer, III, may then be understood in terms of the same type of interactions invoked previously (5,6) to explain the differences in the nmr spectra of these two adducts. Specifically, the marked contrast observed in both the nmr and ir spectra may be due to an enhancement of innate structural differences between the isomers. The evidence for a strong *intra*molecular O-H···N hydrogen-bond such as shown in Figure 1 is based on the magnetic non-equivalence of the "a" and "b" positions observed in the nmr spectra (4-6) of solutions of the adducts in dimethylsulfoxide, a solvent noted for its ability to form strong hydrogen bonds with alcohols (31). The narrower ir absorption in the 3300-2700 cm^{-1} region of the spectrum of IV may be due to both stronger *intra*molecular O-H···N and weaker *inter*molecular N-H···N hydrogen-bonds than in III. We have previously suggested (6) that the former influence may be ascribed to steric repulsion in III between the axial methyl group and ring π-electrons, an influence which is reduced in IV by virtue of the more equatorial position of the carbinol methyl group. If this is indeed the case, then the otherwise sharp band expected at around 3260 cm^{-1} is probably obscured by overlap with a sharper and higher frequency N-H stretching mode than would be expected by analogy to the spectrum of III.

Comparative spectra of adduct II and its tri-deuterated derivative (II-d_3), prepared by repeated recrystallization of II from deuteriomethanol, are shown in Figure 8. Based on the preceding discussion, one might expect the spectrum of the latter to show only three bands in the "O-D, N-D" region (*i.e.*, 2500-2200 cm^{-1}), *viz.*, one band for each N-D stretching mode and one for a single O-D stretching vibration. However, there appear to be at least four, and possibly six, new bands in this region, *viz.*, at 2440, 2380, 2280 and 2160 cm^{-1}, the last being very broad with shoulders at 2190 and 2130 cm^{-1}. In the absence of further studies of this deuterated adduct, it is possible only to conjecture that these "extra" bands are due to the presence of more than one tautomeric form of the adduct in the solid state. The tautomerism apparently involves only the various amine-nitrogen sites, since there is only one band, that at 2440 cm^{-1}, which can be correlated with the presumed O-H band at 3280 cm^{-1} in the spectrum of the protonated species. The existence of more than one tautomeric form of the adducts in the solid state may explain the great difficulty we experienced

in obtaining good crystals of these compounds.

EXPERIMENTAL

Materials.

Purine was obtained from Aldrich Chemical Company and Sigma Chemical Company and was twice recrystallized from methanol and vacuum-dried at 78°. This material was found to be equivalent to another sample purified by vacuum-sublimation: m.p. 217-218° [lit.: 217-218° (32); 212-213° (33)]; decadic molar extinction coefficients at 263 nm: methanol - 7.54 x 10^3 [lit.: 7.35 x 10^3 (34)]; ethanol - 7.60 x 10^3; 2-propanol - 7.63 x 10^3 [lit.: 7.46 x 10^3 (34)]. Purines deuterated at the 6- and 8-positions, respectively, were prepared as described by Schweizer, *et al.* (32). These deuterated products were twice recrystallized from methanol to restore readily exchangeable (*i.e.*, N-H) protons. Purine deuterated at the 7- (or 9-) nitrogen was prepared by repeated precipitation of purine from deuterium oxide by addition of acetone, followed by drying at 120°. The extent of deuteration was not determined. The uv and nmr spectra and melting points of all deuterated purines were compared with those of purine itself. The purine-alcohol photoadducts were prepared as described previously (5,6).

Spectra.

Mass spectra of solid samples were recorded on an Associated Electrical Industries MS-12 mass spectrometer at 70 eV and ionization chamber temperatures of 170-220°. Due to low solubilities in commonly used solvents, the ir spectra were taken on potassium bromide discs (~ 1 mg. sample / 200 mg. potassium bromide). The instrument was a Perkin-Elmer Model 257 double-grating spectrophotometer.

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