yield the diacetate **4f**, mp 180–181°, $[\alpha]D$ +96°, in 90% yield.

3α,20α-Dihydroxy-5β-pregn-9(11)-en-12-one (4g).—Methanolysis of **4f** (280 mg) in methanolic sodium methoxide at reflux for 2 hr yielded the free diol **4g**: mp 222–224°, 235 mg, 95%. The product was recrystallized once from acetone–hexane: mp 226–227°, $[\alpha]D$ +94°, yield 206 mg, 88%.

Anal. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.70; H, 9.76.

3α-Acetoxy-20α-hydroxy-5β-pregn-9(11)-en-20-one (4h).—A solution of **4g** (0.43 g) in pyridine (10 ml) and acetic anhydride (0.26 ml) was allowed to stand at room temperature for 24 hr. The crude product obtained was chromatographed on silica gel. Elution with benzene–acetone (97:3 to 95:5) gave the diacetate **4f** (250 mg, mp 180–182°) in 46% yield. Further elutions with benzene–acetone (93:7) afforded **4h**: mp 157–158° (from methanol–water), $[\alpha]D$ +110°, yield 120 mg, 25%.

Anal. Calcd for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found: C, 73.75; H, 9.12.

3α-Hydroxy-20α-acetoxy-5β-pregn-9(11)-en-12-one (4i).—Partial methanolysis of **4f** (0.62 g) in methanol (30 ml) containing sodium methoxide (3.2 ml of a 2.5% solution) at room temperature for 2 hr was followed by neutralization with dilute hydrochloric acid, dilution with water, and concentration at reduced pressure. The crude **4i** (0.53 g, 94%, mp 172–174°) was purified by column chromatography on silica gel and crystallization from ether–hexane: yield 0.45 g, 80%, mp 177.5–178.5°, $[\alpha]D$ +75°.

Anal. Calcd for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found: C, 73.60; H, 9.11.

The Hemipicrates of 3-Amino- and 3-Methylamino-2-oxazolidinone[1]

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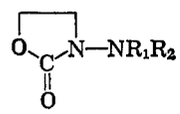
3-Amino-2-oxazolidinone gave a monopicrate or a hemipicrate depending on reaction conditions, while 3-methylamino-2-oxazolidinone gave only a hemipicrate. Conversely, the 3-ethylamino, 3-anilino, and 3-dimethylamino analogs yielded only monopicrates. A number of infrared correlations have been made for the oxazolidinones and their picrates with particular emphasis on hydrogen-bonding effects. It is proposed that in the hemipicrates 1 mole of amine is bound as an amine salt and the second mole is bound by an unusually strong amine–nitro hydrogen bond.

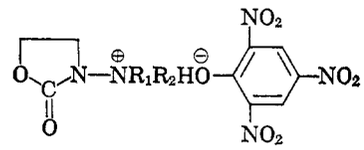
The formation of a hemipicrate between 2 moles of a nitrogen-containing organic compound and 1 mole of picric acid is a known but uncommon reaction. About 50 compounds exhibit this behavior, including aliphatic and aromatic amines, nitrogen heterocycles, and amino-nitrogen heterocycles. Several of these materials also form monopicrates. However, to the best of our knowledge, no attempt to explain the mode of bonding in hemipicrates has been made.

During the course of some work on 3-amino-2-oxazolidinone[2] (I), it was found that I gave both a monopicrate and a hemipicrate. This report describes the preparation of the picrates of I and of several 3-substituted amino-2-oxazolidinones (II–VII). Infrared data have been obtained on the oxazolidinones and their picrates with special emphasis on hydrogen bonding and some postulates have been made on the possible types of bonding in these specific picrates.

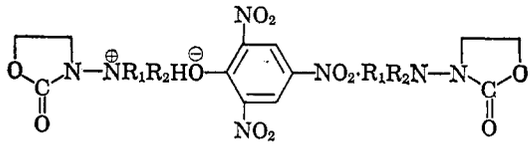


I, $R_1 = R_2 = H$
II, $R_1 = H$; $R_2 = CH_3$
III, $R_1 = H$; $R_2 = C_2H_5$
IV, $R_1 = H$; $R_2 = C_6H_5$
V, $R_1 = H$; $R_2 = COCH_3$
VI, $R_1 = R_2 = CH_3$
VII, $R_1 = R_2 = COCH_3$

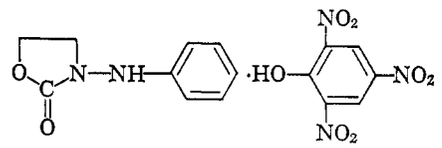
Treatment of I with excess picric acid gave a compound whose infrared spectrum was consistent with an amine salt (VIII). When recrystallization of VIII was attempted from ethanol, the hemipicrate IX was obtained,[3] along with some of the original monopicrate VIII and some free picric acid. The hemipicrate IX was also prepared by the reaction of VIII with I and by the direct reaction of 2 moles of I and 1 mole of picric acid. Conversely, the reaction of IX and picric acid gave VIII.[4] The equimolar reaction of I and picric acid yielded a mixture of both picrates.



VIII, $R_1 = R_2 = H$
XI, $R_1 = H$; $R_2 = C_2H_5$
XII, $R_1 = R_2 = CH_3$



IX, $R_1 = R_2 = H$
X, $R_1 = H$; $R_2 = CH_3$



XIII

The fact that the monopicrate VIII was not completely converted to the hemipicrate IX on heating in ethanol suggested that the buildup of free picric acid might be inhibiting the reaction. This was confirmed when VIII was recrystallized unchanged from ethanol containing 1 equiv of picric acid.

(1) This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, under Contract NOrd 18728, and was monitored by the Bureau of Naval Weapons, RMMP, under Contract NOw 65-0277-c.

(2) G. Gever, U. S. Patent 2,625,402 (1953); *Chem. Abstr.*, **48**, 12179 (1954).

(3) A. L. Remizov and N. V. Khremov-Borisov [*Zh. Obshch. Khim.*, **23**, 794 (1953)] have reported a similar reaction for 4-morpholineacetic acid.

(4) M. de Jong and J. P. Wibaut [*Rec. Trav. Chim.*, **49**, 237 (1930)] have described a similar reaction for pyrrolidine.

The reaction of 3-methylamino-2-oxazolidinone[5] (II) with picric acid gave only a hemipicrate (X). The monopicrate of II was not obtained even using large excesses of picric acid. In contrast, 3-ethylamino-2-oxazolidinone[5] (III) and 3-dimethylamino-2-oxazolidinone[6] (VI) gave only monopicrates, both of which were amine salts (XI and XII). Neither 3-acetamido-2-oxazolidinone[7] (V) nor 3-diacetamido-2-oxazolidinone[5] (VII) reacted with picric acid. 3-Anilino-2-oxazolidinone[8] (IV) also gave only a monopicrate. However, the infrared spectrum of this picrate indicated that it was not a salt but a molecular complex (XIII).

Picric acid is acknowledged to form two different types of compounds with nitrogen bases.[9] Strong bases generally form salts, while the products obtained from weak bases are molecular complexes. These complexes are formulated as arising from the weak interaction of an electron donor with an electron acceptor—in this case picric acid.

At this point, we were interested in trying to correlate the infrared spectra of the various picrates with the different types of bonding present. Before proceeding to this, some data were obtained on the infrared spectra of the free oxazolidinones (Table I).

TABLE I

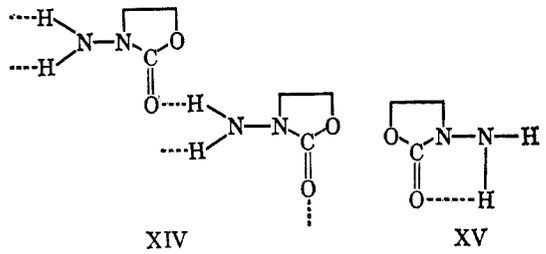
INFRARED SPECTRA (cm^{-1}) OF 3-SUBSTITUTED AMINO-2-OXAZOLIDINONES

	Halocarbon mull		0.01 *M* solution in CCl_4	
Compd	NH	C=O	NH	C=O
I	3338, 3204	1735[a]	3353, 3220	1778[b]
II	3290	1750[c]	3301	1773
III	3287	1756	3297	1771
IV	3292	1751	3310	1782
V	3258	1730	3330	1787[d]
VI	...	1770	...	1771
VII	...	1789	...	1790[d]

[a] NH_2, 1644 cm^{-1}. [b] NH_2, 1624 cm^{-1}. [c] Liquid smear of neat compound. [d] 0.0025 *M*.

The spectra of the oxazolidinones in high dilution in carbon tetrachloride, where intermolecular effects are usually negligible,[10] indicated that the nature of the amino substituent has an effect on the frequency of the carbonyl band. Compared to the unsubstituted amine I, electron-withdrawing substituents (IV, V, VII) raised the carbonyl frequency, and electron-donating substituents (II, III, VI) lowered the carbonyl frequency. This accords with observations on 3-substituted 2-oxazolidinones[11] and probably reflects the inductive effect of the substituents on the electron density of the carbonyl group.[12]

The spectra of the oxazolidinones as mulls indicated that these materials are intermolecularly hydrogen bonded. The spectrum of 3-amino-2-oxazolidinone (I) as a mull showed downward shifts in the NH and carbonyl frequencies and an upward shift in the NH_2 frequency. These shifts are all characteristic of a hydrogen-bonded amine.[13] The fact that these shifts were present also indicated that the hydrogen bonding is primarily intermolecular (XIV) rather than intramolecular (XV). An intramolecular hydrogen bond would be expected to persist in a nonionizing solvent such as carbon tetrachloride, and the resulting spectrum would show no significant changes in band positions.[14]



XIV XV

The similar shifts in the spectra of compounds II–V also showed them to be intermolecularly hydrogen bonded. The disubstituted compounds VI and VII, with no hydrogen capable of forming a hydrogen bond, had essentially the same carbonyl frequencies in a mull and in solution.

It should be pointed out that the electron-donating or -withdrawing properties of the amino substituents produce several competing effects in the pure compounds. For example, while an electron-donating substituent lowers the carbonyl frequency inductively, this same substituent will also raise the electron density on the amino nitrogen, strengthening the nitrogen–hydrogen bond. This tends to decrease the hydrogen-bonding ability of the amino hydrogen and consequently raises the carbonyl frequency. The converse argument holds true for electron-withdrawing groups. The relative magnitude of these competing effects is difficult to evaluate quantitatively. It may be noted, however, that the shifts in carbonyl frequency in going from mull to solution (Δ = 23–57 cm^{-1}) are considerably larger than the shifts in carbonyl frequency produced by the various substituents in solution (Δ = 4–12 cm^{-1}). On this basis, the hydrogen-bonding effect appears to be considerably stronger.

With the spectral data on the oxazolidinones as a background, spectra were taken on the picrates (Table II). Unfortunately, all of these compounds were insoluble in carbon tetrachloride and similar nonpolar solvents. In polar solvents such as chloroform, these

TABLE II

INFRARED SPECTRA OF PICRATES[a]

Compd	NH	$\overset{\oplus}{N}R_1R_2$	C=O
VIII	...	2700, 2900	1738
IX	3346, 3212	2700, 2900	1739, 1789
X	3292	2800	1757, 1786
XI	...	2800	1761
XII	...	2400	1789
XIII	3282	...	1744

[a] Halocarbon mulls; values are given in cm^{-1}.

(5) F. R. Cervi, M. Hauser, G. S. Sprague, and H. J. Troffkin, *J. Org. Chem.*, **31**, 631 (1966).

(6) R. Delaby, F. Brustlein, C. Warolin, and P. Chabrier, *Bull. Soc. Chim. France*, 2056 (1961).

(7) G. Gever and C. J. O'Keefe, U. S. Patent 2,927,110 (1960); *Chem. Abstr.*, **54**, 12158 (1960).

(8) M. Hauser, *J. Org. Chem.*, **31**, 968 (1966).

(9) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 42.

(10) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 74.

(11) S. Pinchas and D. Ben-Ishai, *J. Am. Chem. Soc.*, **79**, 4099 (1957).

(12) N. B. Colthup, L. H. Daly, and S. E. Wiberely, "Introduction to Infrared and Raman Spectroscopy," Academic Press Inc., New York, N. Y., 1964, pp 186–189.

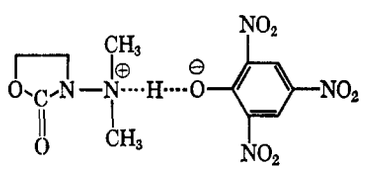
(13) Reference 12, pp 189–190, 242–243.

(14) Reference 10, p 175.

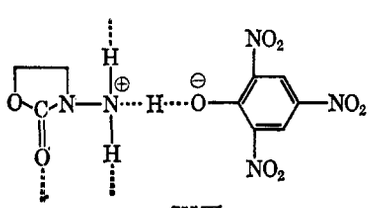
materials dissociated into their original components rather than ions. This was indicated by the reappearance of bands for the starting materials and the disappearance of bands for the picrates. Therefore, all spectral correlations for the picrates had to be made on spectra taken in mulls.

The spectrum of the picrate XII of 3-dimethylamino-2-oxazolidinone (VI) showed that the compound was a tertiary amine salt. A broad band was present at 2400 cm^{-1}, and the carbonyl band was shifted upward compared with the free amine. A band at 2330–2700 cm^{-1} is characteristic of the $NH^{\oplus}$ vibration, and its frequency is sensitive to hydrogen bonding between the ammonium and picrate ions.[15] The position of the band at the lower end of the range (2400 cm^{-1}) in XII indicates the presence of this type of hydrogen bonding (XVI). The upward carbonyl shift in XII, therefore, probably reflects a purely inductive effect by the strongly electron-withdrawing $-\overset{\oplus}{N}H(CH_3)_2$ group, since the single hydrogen of the salt, hydrogen bonded between the ionized amine and hydroxyl, should have little tendency to bond at other sites.

The monopicrates VIII and XI were also found to be amine salts. Bands in the 3200–3500-cm^{-1} region are characteristic of the N–H absorptions of free amines[15] (see Table I), and these were absent in VIII and XI. There were broad bands in the 2700–2900-cm^{-1} region, and these were assigned to the ionized amine. Ionized primary and secondary amines absorb at 2700–3200 cm^{-1} with the position of the band depending upon the extent of ammonium ion–anion hydrogen bonding.[15] The position of these bands at 2700–2900 cm^{-1} in VIII and XI is again indicative of ammonium ion–picrate ion hydrogen bonding (XVII). As with XII, the carbonyl bands in VIII and XI were



XVI



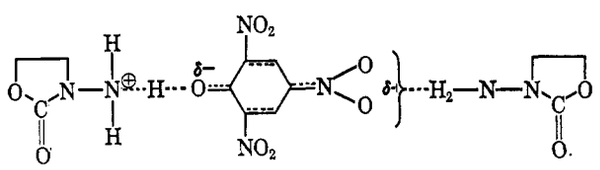
XVII

shifted upwards. However, in both cases the carbonyl shift (Δ = 3 cm^{-1} for VIII and Δ = 5 cm^{-1} for XI) was much smaller than in XII (Δ = 19 cm^{-1}). Ionization of the free amine results in an inductive electron withdrawal raising the carbonyl frequency but this could be balanced by the fact that ionization also renders the amino hydrogens more labile for hydrogen bonding. The increased hydrogen bonding tends to lower the carbonyl frequency and the resultant of the two competing effects is a small upward shift.

In contrast to the spectra of VIII, XI, and XII, the spectrum of the monopicrate XIII still showed absorption characteristic of free NH although the band was shifted slightly downward from its position in the free amine. There were no bands for an ionized amine, and the carbonyl frequency was also shifted slightly downward. Formation of a donor–acceptor complex between the aromatic ring of the anilinooxazolidinone (IV) and picric acid would probably result in slightly greater inductive electron withdrawal from the carbonyl but also in greater hydrogen-bonding ability of the amino hydrogen. Since the over-all carbonyl shift is downward, it would appear that, in this case, the hydrogen-bonding effect is predominant.

The spectra of the hemipicrates IX and X presented a more complex picture with bands for both free N–H and ionized amine as well as two carbonyl bands. From the presence of the bands for an ionized amine it was evident that 1 mole of amine was present as the salt. The nature of the bonding of the second mole of amine was of considerable interest since it was highly unlikely that it was present in a donor–acceptor complex. Salt formation would convert picric acid to the picrate anion which could not function as an electron acceptor.

Compounds I and II—the parent amines of IX and X—did not react with such complex formers as 2,4,6-trinitroanisole, picramide, or 1,3,5-trinitrobenzene. This fact, coupled with the spectral data, suggested the picrate anion was essential to the bonding of the second mole of amine. The acetamido- and diacetamidooxazolidinones (V and VII), which were probably insufficiently basic to form a salt, did not react at all with picric acid. Based on these facts, we felt that the linkage in IX and X might involve hydrogen bonding between the amino hydrogens and the strongly electronegative nitro oxygens (XVIII).



XVIII

The spectrum of IX had a carbonyl band at 1739 cm^{-1} corresponding to the 1738-cm^{-1} carbonyl band of the salt VIII. The continued presence of the $-\overset{\oplus}{N}H_3$ bands at 2700 and 2900 cm^{-1} also showed that IX contained an amine salt and that an ammonium ion–picrate ion hydrogen bond still was present. The position of the free N–H bands at 3346 and 3212 cm^{-1} was below the position of the N–H bands in the solution spectrum of the free amine, indicating that the amino hydrogens of IX were still also participating in hydrogen-bond formation. The second carbonyl band at 1789 cm^{-1} was 10 cm^{-1} higher than the carbonyl band in the solution spectrum of the free amine. This upward shift to a position beyond that of the non-hydrogen-bonded carbonyl of I could arise from an electron-withdrawing effect exerted by the nitro group through the hydrogen bond in XVIII. To some extent the situation is analogous to the carbonyl shift in going from VI to XII.

The spectrum of X exhibited a similar pattern. The carbonyl band at 1757 cm^{-1} probably represents the amine salt judging from the similar position of the carbonyl band in the picrate salt (XI) of the ethyl-

(15) Reference 12, pp 280–282; R. Nuttell, D. Sharp, and T. Waddington, *J. Chem. Soc.*, 4965 (1960).

aminooxazolidinone. The N–H band was below and the second carbonyl band was above the positions of the corresponding bands in the solution spectrum of the free amine.

Further support for amine–nitro hydrogen bonding was obtained from the nitro band region of the infrared spectrum (1500–1600 cm^{-1}). The position of the nitro band in a potassium bromide pellet spectrum of picric acid has been given as 1537 cm^{-1}.[16] We have obtained the same value using a mineral oil mull. On conversion of picric acid to its potassium,[17] sodium, and ammonium salts, this band is shifted to 1570 cm^{-1}. The same 1570-cm^{-1} band is present in the spectra of the monopicrate salts VIII, XI, and XII. However, in the two hemipicrates, IX and X, the position of this band is shifted to 1563 and 1565 cm^{-1}, respectively. The direction of this shift accords with the formation of a hydrogen bond by the nitro group. In contrast, the nitro band is at 1539 cm^{-1} in the spectrum of the molecular complex XIII.

The foregoing infrared data on both IX and X seem to correlate well with the postulated hydrogen band. The formation of amine–nitro hydrogen bonds has been previously described,[18] but such bonds are generally considered to be quite weak. The apparently greater strength of the bonds in IX and X may be a function of the increased charge placed on the nitro oxygens by ionization of picric acid.

The failure of II to form a monopicrate, with its implication of stronger hydrogen bonding by II than I, is amenable of several possible explanations. Assuming that the methylamine II is more basic than the unsubstituted amine I owing to the inductive effect of the methyl group, the salt of II should be more dissociated than the corresponding salt of I. This, in turn, would result in a higher electron density on the nitro groups of the picrate anion and consequently greater hydrogen-bonding ability. However, if this is the case, it would be expected that the ethylamine III would form a stable hemipicrate. In fact, III forms only a picrate salt. At present, we do not feel that we can offer a wholly adequate explanation for these phenomena.

Experimental Section[19]

Picrate of I (VIII).—A solution of 0.63 g (0.006 mole) of I and 2.7 g (0.012 mole) of picric acid in 25 ml of absolute alcohol was allowed to stand 1 hr at 25° and then was refrigerated overnight. The precipitate was filtered and recrystallized from absolute alcohol containing 1.35 g (0.006 mole) of picric acid. Compound VIII (1.93 g, 97%) was obtained as yellow cuboids, mp 113.5–115°.

Anal. Calcd for $C_9H_9N_5O_9$: C, 32.6; H, 2.7; N, 21.2; mol wt, 331. Found: C, 32.9; H, 2.8; N, 21.2; mol wt, 327.

When recrystallization of 0.47 g of VIII was attempted from ethanol not containing picric acid, there was obtained 0.21 g of the hemipicrate IX (see below), 0.08 g of VIII, and 0.16 g of picric acid.

Hemipicrate of I (IX). A. From I.—A solution of 1.25 g (0.012 mole) of I and 1.37 g (0.006 mole) of picric acid in 75 ml of absolute alcohol was allowed to stand several hours at 25°. The precipitate was filtered and recrystallized from absolute alcohol to give 2.57 g (98%) of IX, yellow needles, mp 123–124°.

Anal. Calcd for $C_{12}H_{15}N_7O_{11}$: C, 33.3; H, 3.5; N, 22.6; mol wt, 433. Found: C, 33.5; H, 3.3; N, 22.5; mol wt, 431.

B. From VIII.—A solution of 0.10 g (0.001 mole) of I and 0.33 g (0.001 mole) of VIII in 15 ml of absolute alcohol was allowed to stand several hours at 25°. Filtration gave 0.43 g (100%) of IX.

Conversion of IX to VIII.—A solution of 0.43 g (0.001 mole) of IX and 0.23 g (0.001 mole) of picric acid in 10 ml of absolute alcohol was allowed to stand 1 hr at 25° and then chilled overnight. Filtration gave 0.60 g (91%) of VIII.

Equimolar Reaction of I and Picric Acid.—A solution of 1.25 g (0.012 mole) of I and 2.74 g (0.012 mole) of picric acid in 75 ml of absolute alcohol was allowed to stand 2 hr at 25° and then filtered to yield 1.41 g (54%) of IX. Overnight refrigeration of the filtrate gave 1.49 g (38%) of VIII.

Hemipicrate of II (X).—A solution of 1.16 g (0.01 mole) of II and 1.15 g (0.005 mole) of picric acid in 100 ml of absolute alcohol was allowed to stand 2 hr at 25°. Filtration and recrystallization from absolute alcohol gave 2.21 g (96%) of X, yellow needles, mp 132–133°.

Anal. Calcd for $C_{14}H_{19}N_7O_{11}$: C, 36.4; H, 4.1; N, 21.2; mol wt, 461. Found: C, 36.5; H, 4.1; N, 21.4; mol wt, 458.

Picrate of III (XI).—A solution of 1.30 g (0.01 mole) of III and 2.29 g (0.01 mole) of picric acid in 25 ml of absolute alcohol was allowed to stand 24 hr at 25°. There was no precipitate on chilling. Evaporation of the alcohol gave a viscous, yellow oil which crystallized on standing. Recrystallization from benzene yielded 2.75 g (77%) of XI, yellow cuboids, mp 98–100°.

Anal. Calcd for $C_{11}H_{13}N_5O_9$: C, 36.8; H, 3.6; N, 19.5. Found: C, 36.7; H, 3.9; N, 19.4.

Picrate of IV (XIII).—A solution of 1.78 g (0.01 mole) of IV and 2.29 g (0.01 mole) of picric acid was allowed to stand 2 hr at 25° and then chilled overnight. Filtration, followed by recrystallization from benzene, gave 3.07 g (75%) of XIII, small orange needles, mp 76–77°.

Anal. Calcd for $C_{15}H_{13}N_5O_9$: C, 44.2; H, 3.2; N, 17.2. Found: C, 44.3; H, 3.3; N, 17.4.

Picrate of VI (XII).—A solution of 0.13 g (0.001 mole) of VI and 0.23 g (0.001 mole) of picric acid in 5 ml of absolute alcohol was allowed to stand 2 hr at 25° and then chilled overnight. Filtration and recrystallization from benzene gave 0.30 g (83%) of XII, yellow cuboids, mp 88–89.5°.

Anal. Calcd for $C_{11}H_{12}N_5O_9$: C, 36.8; H, 3.6; N, 19.5. Found: C, 37.1; H, 3.8; N, 19.3.

In the preceding four preparations, variation in the mole ratios of the reactants did not alter the reaction products.

Infrared Spectroscopic Techniques.—Infrared spectra were determined on a Perkin-Elmer Model 521 grating infrared spectrophotometer. Spectra of solids were taken as mulls in a perfluorinated hydrocarbon using sodium chloride plates. Carbon tetrachloride for solution spectra was reagent grade dried over phosphorus pentoxide. Cells of 1-mm thickness gave good resolution of the carbonyl region and 8–10-mm cells gave good resolution of the N–H region. Peaks could be reproduced to ± 1 cm^{-1}.

In solution spectra, dilution below 0.01 *M* produced no significant band shifts.

Acknowledgments.—The author is indebted to Dr. T. H. Brownlee, Dr. G. S. Sprague, and Dr. S. F. Stafiej for a number of valuable suggestions, and to Mr. N. M. Colthup for aid in the interpretation of infrared spectra.

(16) B. Franck, H. Hormann, and S. Scheibe, *Ber.*, **90**, 330 (1957).

(17) The frequency of this band in potassium picrate has been given at 1563 cm^{-1} [L. K. Dyall, *Australian J. Chem.*, 493 (1961)], but it is felt that this is experimental difference since the published spectrum differs from ours by several wavenumbers at all points.

(18) M. Josien and N. Fuson, *J. Chem. Phys.*, **22**, 1169 (1954); L. J. Bellamy, H. E. Hallam, and R. L. Williams, *Trans. Faraday Soc.*, **54**, 1120 (1958); L. J. Bellamy and H. E. Hallam, *ibid.*, **55**, 220 (1959).

(19) Melting points were taken on a Fisher-Johns apparatus and are corrected. Microanalyses were by Research Service Department, Central Research Division, American Cyanamid Co.