Ultraviolet and Infrared Spectra of Cupferron and Neocupferron

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(Received September 6, 1971)

N-nitroso-*N*-phenylhydroxylamine, *N*-nitroso-α-naphthylhydroxylamine, and their sodium salts have been prepared from the ammonium salt of *N*-nitroso-*N*-phenylhydroxylamine (cupferron) and the ammonium salt of *N*-nitroso-α-naphthylhydroxylamine (neocupferron) respectively. The measurements of the UV spectra in solution and the IR spectra with Nujol mull have been carried out on these compounds, including their ammonium salts. The solvent effect and the deuteration effect on the IR spectra have also been examined for the compounds with a hydroxyl group. The formation of a rather strong hydrogen bonding in these aromatic nitrosohydroxylamines has been confirmed from the deuteration effect on the IR spectra and from the solvent effect on the UV and IR spectra. These compounds and their salts have shown the absorption band considered to be a charge-transfer band in the UV spectra, and they have also shown the N=O stretching mode between 1450 and 1468 cm^{-1} corresponding to those of nitrosamines in the IR spectra with the HCB mull.

Ammonium salts of *N*-nitroso-*N*-phenylhydroxylamine and *N*-nitroso-α-naphthylhydroxylamine, which are called cupferron and neocupferron respectively, are well known as analytical reagents for various metallic ions, such as those of transition elements and rare earth elements.[1] They coordinate the metallic ion as a bidentate ligand, forming a chelate which is less soluble in water. In spite of their usefulness, however, few investigations have been made on the molecular structure and the spectroscopic properties of these compounds. For cupferron, some data on the ultraviolet and infrared spectra were reported by Piskorz and Urbanski, but without any detailed analysis.[2] On the other hand, the spectroscopic properties of other *N*-nitroso compounds, nitrosamine and nitrosohydroxylamine have been investigated by many workers. Haszeldine *et al.* carried out a systematic study of the ultraviolet and infrared spectra of *N*-nitroso compounds, and pointed out that the $n\rightarrow\pi^*$ band of the nitroso group usually observed with nitrosamines was absent in the ultraviolet spectra of *N*-alkyl-*N*-nitrosohydroxylamine.[3,4] Bellamy *et al.* and Williams *et al.* investigated the solvent effect of infrared absorption bands for various nitrosamines and assigned some absorption bands to the N=O, N–N, and C–N stretching vibrations.[5,6] Because there is a possibility of inter- or intra-molecular hydrogen bondings between the nitroso group and the hydroxyl group in nitrosohydroxylamines, the ultraviolet and infrared spectra may be very complicated.

The present paper will report on the ultraviolet and infrared spectra of cupferron, neocupferron, and related compounds, as well as on the deuteration effect for the hydroxyl group in *N*-nitrosophenylhydroxylamine and the solvent effect in various organic solvents on the infrared spectra.

1) F. J. Welcher, "Organic Analytical Reagents," Vol. III, Chap. XIII (1955), p. 354.
2) M. Piskorz and T. Urbanski, *Bull. Acad. Pol. Sci.*, **11**, 597 (1963).
3) R. N. Haszeldine and J. Jander, *J. Chem. Soc.*, **1954**, 691.
4) R. N. Haszeldine and B. J. H. Mattinson, *ibid.*, **1955**, 4172.
5) L. J. Bellamy, C. P. Conduit, R. J. Pace, and R. L. Williams, *Trans. Faraday Soc.*, **55**, 1677 (1959).
6) R. L. Williams, R. J. Pace, and G. J. Jeacocke, *Spectrochim. Acta*, **20**, 225 (1964).

Experimental

Materials. Cupferron, which will be designated by NH_4cupf hereafter (Nakarai Chemicals, Ltd., GR grade), was purified by recrystallization from methanol. Neocupferron, which will be designated by NH_4ncupf hereafter (Fluka AG. Buchs SG, Switzerland), was purified by recrystallization from a mixed solvent of methanol and ethyl ether. Since cupferron, neocupferron, and related compounds gradually decomposed in air and in solution at room temperature, all the operations during the syntheses and purification were carried out with the solutions kept at the temperature of ice. All the other reagents were of a GR grade and were used without further purification.

N-*Nitroso*-N-*phenylhydroxylamine (Hcupf)*: Ten milliliters of a 6N hydrochloric acid solution was added to an aqueous solution of NH_4cupf (10 g in 100 m*l* of H_2O). The white-colored precipitant was filtered and repeatedly washed with water. The product was purified several times by recrystallization from acetone and dried in a vacuum. The Hcupf thus obtained was very soluble in organic solvents, but was only slightly soluble in water. The Hcupf was very unstable in both air and organic solvents at room temperature.

Found: C, 51.88; H, 4.18; N, 20.29%. Calcd: C, 52.18; H, 4.38; N, 20.21%.

N-*Nitroso-α-naphthylhydroxylamine (Hncupf)*: The preparation of Hncupf was carried out in the same way as in the case of Hcupf. Hncupf was thus obtained as faint yellow-colored crystals and was less stable than Hcupf. The solubility of Hncupf in a solvent was found to be nearly same as that of Hcupf.

Found: C, 65.21; H, 4.14; N, 14.08%. Calcd: C, 63.82; H, 4.29; N, 14.89%.

Na Salt of Hcupf (Nacupf): NH_4cupf (1.6 g) was dissolved in a 1N NaOH solution (10 m*l*). The solution was heated for several hours at about 80°C and then cooled to room temperature. The white crystals thus precipitated were then recrystallized from a water-acetone mixed solvent. The Nacupf was very soluble in water, but was insoluble in organic solvents.

Found: C, 45.18; H, 3.13; N, 17.37%. Calcd: C, 45.01; H, 3.15; N, 17.50%.

Na Salt of Hncupf (Nancupf): The preparation of Nancupf was carried out in the same way as in the case of Nacupf. This salt was recrystallized from acetone. The Nancupf, obtaned as faintly-yellow-colored crystals, was very soluble in water, slightly soluble in polar organic solvents, such as acetone and methanol, and insoluble in non-polar solvents. The Nancupf was slightly hygroscopic. From the results of

chemical analysis and infrared spectroscopy, this salt was confirmed to be a hydrate.

Found: C, 55.13; H, 3.25; N, 12.98%. Calcd for Nancupf·$\frac{1}{2}H_2O$: C, 54.80; H, 3.68; N, 12.78%.

Deuteration of Hcupf. The deuteration of Hcupf was carried out by recrystallizing Hcupf seven times from an acetone-D_2O mixed solvent in an argon gas atmosphere while cooling in ice water. Before the deuteration, the acetone was dried by bubbling in argon gas. The product thus obtained was, however, partly deuterated Hcupf. D_2O (99.5%) by E. Merck was used.

Measurements. The ultraviolet spectra and infrared absorption spectra were recorded on a HITACHI ESP-3T type and a HITACHI-PERKIN-ELMER Model 225 type IR grating spectrophotometer respectively, where Nujol mull, HCB mull, and solution techniques were used. Most of the solvents in the UV and IR measurements were spectrograde reagents (E. Merck and Nakarai Chemicals, Ltd.). Since both the Hcupf and Hncupf were very unstable in solutions, it was impossible to determine the concentration of the solution in the IR measurements. Deuterated Hcupf was treated in a N_2 atmosphere.

Results and Discussion

UV Spectra. The ultraviolet spectra of Hcupf and Nacupf are shown in Figs. 1 and 2 respectively. In Table 1 are tabulated the wavelengths and molar extinction coefficients of the absorption maxima and minima observed with various solvents. The absorption spectra of Nacupf and NH_4cupf are similar to each other, but are different from those of Hcupf. The 290 mμ band observed with Nacupf and NH_4cupf shifts to 260 mμ for Hcupf, and the 220 mμ band of the former shifts to a shorter wavelength for the latter, where the band appears as a shoulder. The 220 mμ band of Nacupf and NH_4cupf and the 260 mμ band of Hcupf do not show any remarkable solvent effects, but the 290 mμ band of the former is sensitive to solvents, *i.e.*, it shows a blue shift with the change of the solvent from

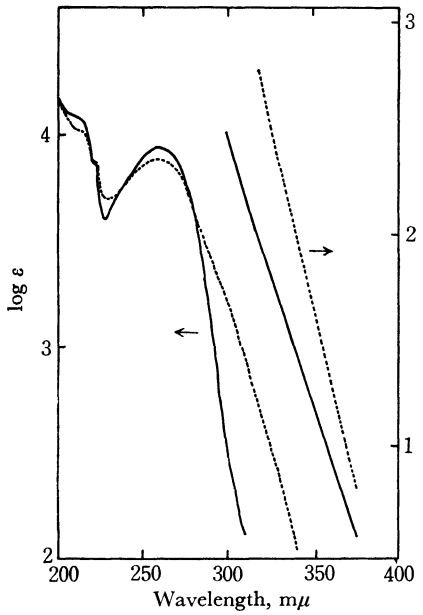


Fig. 1. UV spectra of Hcupf in *n*-heptane (——) and in methanol(------).

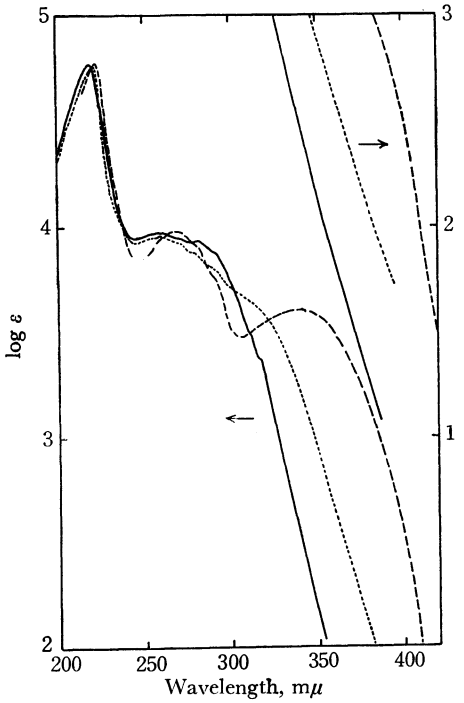


Fig. 2. UV spectra of Nancupf in water(——), in ethanol (------), and in tetrahydrofuran(-----).

alcohol to water. The 260 mμ band of Hcupf or the 290 mμ band of NH_4cupf and Nacupf is not present in *N*-alkyl-*N*-nitrosohydroxylamine,[3] but it is too intense to be identified as originating only from the $A_{1g}\rightarrow B_{2u}$ transition band of benzene. Since the nitroso group is a strong electron acceptor,[7] and since the hydroxyl group as well as the phenyl ring are electron donors, this band is considered to be essentially a charge-transfer band generally sensitive to solvents. That it is insensitive to solvents for Hcupf is looked upon as being due to the presence of strong hydrogen bonding. The shoulder around the 210 mμ of Hcupf and the 220 mμ bands of NH_4cupf and Nacupf may be assigned to be the $A_{1g}\rightarrow B_{1u}$ transition band of the benzene ring, since it shows little solvent effect.

The spectra of Hncupf, Nancupf, and NH_4ncupf are very similar to each other and may all be considered to originate mainly from the naphthyl group, though the 339 mμ band for Nancupf in THF is not found in the others. The band around 220 mμ corresponds to the $A_{1g}\rightarrow E_{1u}$ transition; the band around 280 mμ with a structure to the $A_{1g}\rightarrow B_{1u}$ transition, and the 329 mμ band observed as a shoulder, to the $A_{1g}\rightarrow B_{2u}$. Though Hncupf is also considered to form hydrogen bonding, its effect upon the UV absorption spectra is not observed. For Nancupf and NH_4ncupf, a new band appears as a shoulder around 310 mμ when they are dissolved in ethanol; for Nancupf, this band is shifted to a longer wavelength as the polarity of the solvent decreases, finally resolving into a single peak at 339 mμ with THF. This band is considered to correspond to the 260 mμ band of Hcupf and can be assigned to the charge-transfer band. Thus the bands around 280 mμ

7) M. Tanaka, J. Tanaka, and S. Nagakura, This Bulletin, **39**, 766 (1966).

Table 1. Ultraviolet spectra of Hcupf, Hncupf, and their salts

Compounds	Solvent	λ_{max} in mμ (log ε)	λ_{min} in mμ (log ε)
Hcupf	*n*-heptane		227 (3.60)
		259.5 (3.95)	
	CCl_4	261 (3.96)	
	$CHCl_3$	260 (3.97)	
	THF		230 (3.68)
		260 (3.93)	
	C_2H_5OH		229 (3.68)
		258.5 (3.90)	
	CH_3OH		230 (3.70)
		259 (3.89)	
NH_4cupf	C_2H_5OH		212 (3.94)
		222 (4.00)	
			249 (3.56)
		298.5 (3.87)	
	CH_3OH	222 (4.03)	
			249 (3.35)
		293 (3.96)	
	H_2O	219 (4.03)	
			244 (3.50)
		284 (4.00)	
Nacupf[a]	50% CH_3OH,		210 (3.98)
	50% H_2O	221.5 (4.06)	
			246 (3.43)
		289 (4.03)	
	H_2O		209.5 (4.00)
		219.5 (4.05)	
			244 (3.52)
		283.5 (4.02)	
Hncupf[a]	*n*-heptane	218.5 (4.70)	265 (3.66)
		293 (3.80) str.	
	$CHCl_3$		268 (3.66)
		294 (3.77) str.	
	THF	218.5 (4.66)	
		291 (3.80) str.	
	CH_3OH	217.5 (4.74)	
			264 (3.74)
		282 (3.80) str.	
NH_4 ncupf[a]	C_2H_5OH	219.5 (4.74)	
			250 (3.88)
		261 (3.89) str.	
	CH_3OH	220.5 (4.71)	
			247 (3.90)
		260 (3.92) str.	
	H_2O	219.5 (4.77)	
			245 (3.95)
		260 (3.97) str.	
Nancupf[a]	THF	222.5 (4.78)	
			247 (3.83)
		269 (3.98) str.	
			306 (3.48)
		339 (3.61)	
	C_2H_5OH	221 (4.75)	
			245 (3.92)
		260 (3.96) str.	
	50% CH_3OH,	220.5 (4.75)	
	50% H_2O		246 (3.92)
		260 (3.94) str.	
	H_2O	219.5 (4.77)	
			244 (3.94)
		260 (3.97) str.	

a) The spectra of these compounds exhibited a structure between about 260 and 300 mμ, and in the table their absorption maxima are shown.
"str." is an abbreviation for the appearance of a structure in the absorption band.

of Hncupf, NH_4ncupf, and Nancupf seem to consist of the $A_{1g} \rightarrow B_{1u}$ transition of naphthalene superposed on the charge-transfer transition.

The Lack of $n \rightarrow \pi^*$ Bands in the UV Region. Hcupf and its salts are white in the polycrystalline state and colorless in solution. Hncupf and its salts are faintly yellow both in the polycrystalline state and in solution. *C*-nitroso compounds are also colorless or pale yellow in the crystalline form, in which they exist as a dimer, but their monomer in solution is green or blue. Most of the nitrosamine derivatives are known to be yellow in the liquid state.[3,4] The color of the monomer *C*-nitroso compounds and nitrosamine derivatives originates from the $n \rightarrow \pi^*$ transition bands of the nitroso group, which are observed in the nitrosamine derivatives around 350 mμ and in the monomer of *C*-nitroso compounds around 700 mμ.[8,9] Generally, in *N*-nitroso compounds there was no absorption band corresponding to the 700 mμ band appearing in monomer *C*-nitroso compounds, a band which is interpreted as one of the $n \rightarrow \pi^*$ transition bands that originate from the excitation of a non-bonding electron of the nitrogen atom to the anti-bonding π^* orbital. In order to explain this phenomenon, Haszeldin assumed that the non-bonding electron of the nitrogen atom in the nitroso group might be used to form the dimer, just as in the case of the dimer of *C*-nitroso compounds.[3,4] The presence of dimers in *N*-nitroso compounds, however, has been denied by Williams *et al.* and by Layne *et al.* on the basis of IR and UV measurements respectively.[6,10] Since it is impossible for cupferron, neocupferron, and their salts to be dimerized at the nitrogen atoms of nitroso groups because of the steric hindrance, the $n \rightarrow \pi^*$ transition band near 700 mμ could appear according to the assumption by Haszeldin *et al.* Nevertheless, no absorption bands are observed near 700 mμ in these compounds, just as in the case of other *N*-nitroso compounds.

In the spectra of Hcupf, Hncupf, and their salts, the $n \rightarrow \pi^*$ transition band around 350 mμ is also absent, although it is usually observed in nitrosamine derivatives. As for the reason why this is absent in the spectra of *N*-nitrosohydroxylamine, Haszeldin *et al.* suggested the possibility of inter- or intra-molecular hydrogen

8) B. G. Gowenlock and W. Luttke, *Quart. Rev.* (London), **12**, 321 (1958).
9) K. Nakamoto and R. E. Rundle, *J. Amer. Chem. Soc.*, **78**, 1113 (1956).
10) W. S. Layne, H. H. Jaffe, and H. Zimmer, *ibid.*, **85**, 435 (1963).

TABLE 2. INFRARED SPECTRA OF Hcupf, Hncupf, AND THEIR SALTS (Nujol and HCB mull)

Hcupf	NH_4cupf	Nacupf	Tentative assignment	Hncupf	NH_4ncupf	Nancupf	Tentative assignment
	1675 W, b			1598 M	1595 M	1597 M	ν(C=C)
1587 W	1589 M	1588 M	ν(C=C)	1506 M	1508 M	1510 M	
1487 S	1481	1481 S		1480 W			
1468 VS	1459 VS	1455 S	ν(N=O)	1460 sh	1460 sh	1460 W	
	1455 S			1450 S	1446 S	1440 W	ν(N=O)
	1422 S		$\nu_4(NH_4^+)$		1390 M	1396 M	
1397 sh			δ(OH)	1379 VS		1379 VW	
1382 S				1350 M	1351 VW	1357 M	
1338 M	1331 S	1341 VS			1324 M	1322 VS	
1303 S	1316 S	1312 S		1309 W			
1280 S	1264 VS	1265 VS			1295 VS	1297 S	
	1220 VS	1226 VS			1280 sh	1280 sh	
		1202 VW		1272 VW			
1167 M	1168 W	1166 M	phenyl	1256 S			
1158 M	1160 M			1217 W	1219 VS	1222 S	
1110 S	1104 VW	1105 VW	phenyl	1198 M	1190 M	1198 VS	
1097 W	1071 M	1073 M			1170 sh	1163 M	
1063 VS	1056 S	1058 S	ν(NH)	1149 VW	1148 VW	1143 W	
1019 VS	1020 M	1019 W	δ(CH)	1141 W	1125 M	1133 W	
1003 W				1081 sh			
993 VW				1069 VS	1064 W	1061 W	
	971 VW	967 W		1021 M	1019 W	1019 W	δ(CH)
922 VS	907 VS	907 VS	ν(N–O)	998 M	981 M	983 S	ν(NN)
		850 W		950 VW	943 VW		
	773 VW			911 S	905 VS	902 VS	ν(N–O)
763 VS	761 VS				895 M		
	755 VS	752 VS	γ(CH)		852 VW	853 VW	
742 S, b			γ(OH)	858 W	865 VW	864 VW	
713 S, b					817 M	815 S	γ(CH) 3 adj. H
	722 VW	720 VW		808 S	799 S	798 VS	
686 sh	695 sh	695 S		796 VS	789 VS	790 S	
680 VS	689 VS	683 VS		762 VS	769 VS	765 VS	γ(CH) 4 adj. H
647 S			δ(NNO)		758 S		
	615 VW	616 W		740 VW	735 VW	742 VW	
	581 M	584 S	δ(NNO)		721 VW	720 VW	
	514 W	522 M		684 S			γ(OH)
482 M	470 W	458 M		664 M			
406 W				654 S	662 M	663 M	δ(NNO)
393 M				630 W	636 W	647 W	
371 M	370 M	376 S		570 M	571 M	574 sh	
	305 VW	303 VW				530 S, vb	γ(OH)
	262 M	262 M		527 W	529 W		
				521 VW			
				463 VW			
				450 W	448 VW	453 W	
				430 W		425 W	
				413 M			

Abbreviations: V, very; S, strong; M, medium; W, weak; b, broad; sh, shoulder; ν, stretch; δ, in-plane deformation; γ, out-of-plane deformation.

bonding.[3] As will be discussed later, Hcupf and Hncupf are considered to form hydrogen bonding, but in Nacupf and Nancupf there is no possibility of forming hydrogen bonds. As a reason for the absence of the $n\rightarrow\pi^*$ transition band for *N*-nitrosohydroxylamine, there seems to be a possibility that the $n\rightarrow\pi^*$ band may be hidden by the intense bands of the shorter-wavelength side.

The Hcupf is very unstable in organic solvents; for example, it gradually decomposes into the green solution of *C*-nitroso compounds, meanwhile forming some colorless gas and a water-soluble precipitant. This solution exhibits absorption maxima at 283 mμ, 305 mμ, and 760 mμ, showing the formation of nitrosobenzene.[11,12]

11) C. N. R. Rao and K. R. Bhaskar, "The Chemistry of the Nitro and the Nitroso Groups," Part I, ed. by H. Feuer, Interscience Publishers, New York, Chap. III (1969), p. 137.

12) K. Tabei and S. Nagakura, This Bulletin, **38**, 965 (1965).

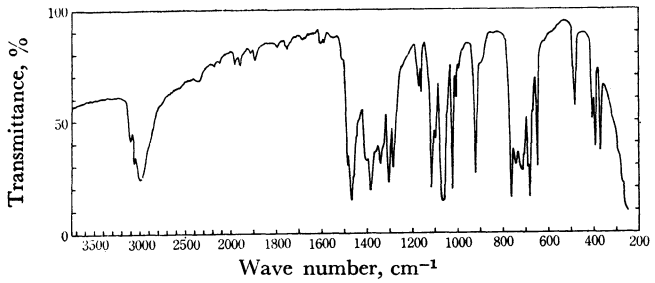


Fig. 3. IR spectrum of Hcupf. 200—1350, 1500—2700 cm^{-1}: Nujol mull, 1350—1500, 2700—4000 cm^{-1}: HCB mull.

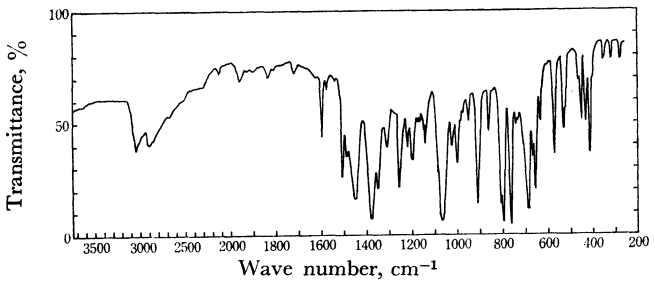


Fig. 4. IR spectrum of Hncupf. 200—1350, 1500—2700 cm^{-1}: Nujol mull, 1350—1500, 2700—4000 cm^{-1}: HCB mull.

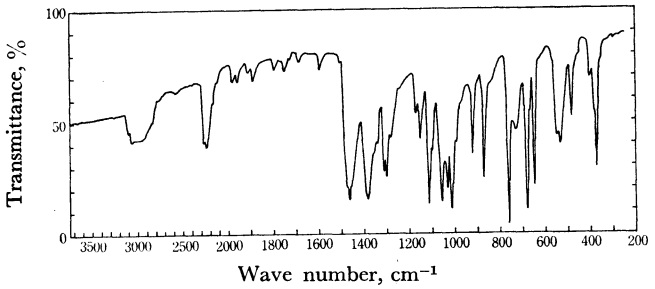


Fig. 5. IR spectrum of deuterated Hcupf. 200—1350, 1500—2700 cm^{-1}: Nujol mull, 1350—1500, 2700—4000 cm^{-1}: HCB mull.

It may be considered, therefore, that the strength of the N–N bond in Hcupf is relatively week.

IR Spectra. In Figs. 3—5 are shown the IR spectra of Hcupf, Hncupf, and partly deuterated Hcupf respectively. The peak wave numbers of the IR spectra and the tentative assignments of each band are tabulated in Table 2. All the compounds exhibited absorption bands corresponding to the vibrations of the aromatic ring, such as 690 and 750 cm^{-1} of the CH out-of-plane deformation, characteristic of the mono-substituted benzene. Particularly in the region between 1700 cm^{-1} and 1000 cm^{-1}, however, the spectra were very complicated by possible interactions between the substituent vibration and the aromatic-ring vibration. In this region, the spectra of the ammonium salts and sodium salts were very similar to each other, but the spectra of compounds with hydroxyl groups were different from those of the salts, just as was observed in the UV spectra. In the frequency region higher than 1700 cm^{-1} these appeared intense bands originating from the vibrations of CH stretching (benzene) and OH stretching, and from the NH_4^+ ion vibrations, which will be discussed later. Since Hcupf and Hncupf are soluble in various organic solvents, the measurement for solvent effects was carried out; the data obtained for the main peaks are shown in Tables 3 and 4, where it may be seen that most absorption peaks either shift to a slightly lower wave number side with the increasing polarity of solvents or are insensitive to solvents.

The bands around 1460 cm^{-1} and 1060 cm^{-1} of Hcupf and its salts were assigned to the N=O and the N–N stretching modes respectively, analogously with those of the nitrosamines. These bands of Hcupf were observed on a higher frequency side than the corresponding ones of Nacupf and NH_4cupf, and they scarcely shifted with the polarity of the solvents. This behavior is different from that of the nitrosamines, in which $\nu_{N=O}$ shifts to a lower frequency, and ν_{N-N}, to a higher frequency, with the increasing polarity of

Table 3. Frequencies, cm^{-1}, of Hcupf in various solvents

Solvent[a)]	Frequencies, (cm^{-1})									
Cyclohexane	—	—	—	—	1105	1067	—	920	753	—
Carbontetrachloride	1467	1388	1305	1273	1107	1066	1021	921	—	705
Carbondisulfide	—	1390	1305	1272	1105	1063	1022	920	759	700
Benzene	—	—	1305	1275	1105	—	—	920	756	—
Methyliodide	—	—	—	—	1106	1063	1020	—	762	706
Methylenechloride	—	1387	—	—	1106	1070	1022	921	—	—
Chloroform	1463	1387	1307	—	1107	1064	1021	919	—	—
Methylenebromide	1464	—	1304	1270	1100	1060	1020	921	763	—
Bromoform	1467	1388	1303	1266	—	1061	1020	921	762	—
Methyleneiodide	1464	—	1302	1265	—	—	—	920	762	—

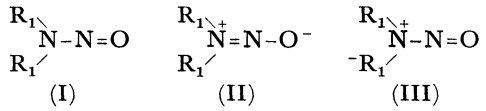
a) The polarity of the solvent increases from cyclohexane to methylene iodide.

Table 4. Frequencies, cm^{-1}, of Hncupf in various solvents

Solvent[a)]								
Carbontetrachloride	1448	1250	1074	1062	998	912	—	656
Carbondisulfide	—	1254	1074	1062	998	911	766	656
Methylenebromide	1436	—	1070	1059	999	912	769	—
Methyleneiodide	1435	1252	—	—	998	912	768	657

a) The polarity of the solvent increases from carbon tetrachloride to methylene iodide.

solvents. According to Williams *et al.*,[6] the solvent effect of nitrosamines can be explained by assuming the following resonance structures:

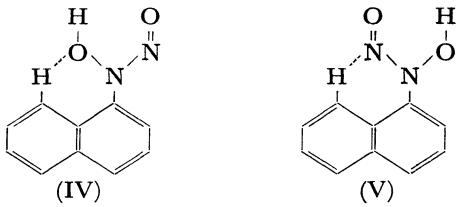


(I) (II) (III)

If the polarity of the solvents increases, the contribution of the structure II will increase, thus giving rise to a lowering of the frequency of N=O stretching vibration and a raising of the frequency for N–N. The reason why Hcupf, contrary to the case of nitrosamines, did not exhibit the solvent effect is considered to be that the relatively strong hydrogen bonding in Hcupf leading to a dimer may exclude the resonance structures which are sensitive to solvents. The large shift of the strong band assigned to the N–N=O deformation mode from 581 cm^{-1} for NH_4cupf and from 584 cm^{-1} for Nacupf to 647 cm^{-1} for Hcupf could also be due to the formation of hydrogen bonding in Hcupf.

In the partly-deuterated Hcupf, the intensity of the broad absorption bands at 713 and 743 cm^{-1} of Hcupf, which are absent in NH_4cupf and Nacupf, is much decreased and strong new broad bands are found at 531 and 548 cm^{-1}. Thus the bands at 713 and 743 cm^{-1} can be assigned to the γ_{OH} mode, and those at 531 and 548 cm^{-1}, to the γ_{OD} mode. The new band at 1030 cm^{-1} can be attributed to the δ_{OD} mode, and the corresponding δ_{OH} band, which is expected to appear near 1400 cm^{-1}, is observed as a shoulder at 1397 cm^{-1}. Deuteration also affects the frequency of the N–O stretching vibration, which appears as a strong and characteristic band at 922 cm^{-1} in Hcupf (at 907 cm^{-1} in NH_4cupf and Nacupf). In the deuterated Hcupf, the intensity of the band at 922 cm^{-1} was decreased and at 873 cm^{-1} there was found a strong new band which was considered to be the N–O band shifted to a lower frequency by the deuteration. A new band found at 1153 cm^{-1} has not yet been assigned.

In Hncupf and its salts, the bands of the CH out-of-plane deformation, being characteristic of α-substituted naphthalene, are found around 800 cm^{-1} and 750 cm^{-1}. The band at the former wave number is due to three adjacent ring hydrogen atoms, while the band at the latter is due to four adjacent ring hydrogen atoms. Each band of them is split into two or three subbands in the spectra measured with Nujol mull. As the splitting of the band around 800 cm^{-1} was observed even in the CS_2 solution, this splitting is considered not to be due to the inter-molecular interaction, but it may originate from the interaction between a ring hydrogen and substituents as follows:



(IV) (V)

The bands around 1450 cm^{-1} and 990 cm^{-1} can be assigned to the N=O and N–N stretching modes respectively, just as in the case of cupferrons. In the neocupferrons, the band of N=O stretching mode is lowered in frequency and decreased in intensity compared to that of cupferrons. This behavior may be explained by a weakening of the double-bond character due to the increase in the electron-accepting property of the naphthyl group and the contribution of the structure V. The band of the N–O stretching mode is found around 900 cm^{-1} at nearly the same wave number as in the cases of the Hcupf and its salts.

IR Spectra in the Frequency Region Higher than 1700 cm^{-1}. Figure 6 shows the spectra of Hcupf and deuterated Hcupf between 2000 and 3500 cm^{-1} as measured with the HCB mull and in a CCl_4 solution. The broad band of Hcupf observed with the maximum at 2980 cm^{-1} (solid) can be assigned to the bonded OH stretching mode. In the deuterated Hcupf it is weakened, however, and a new band is found with maxima around 2240 and 2260 cm^{-1}. Both bands can be assigned to the bonded OD stretching mode. In a CCl_4 solution these ν_{OH} and ν_{OD} bands shift to a lower frequency side by 70 cm^{-1} and 100 cm^{-1} respectively. In the Hncupf, however, the broad band with the maximum at 2910

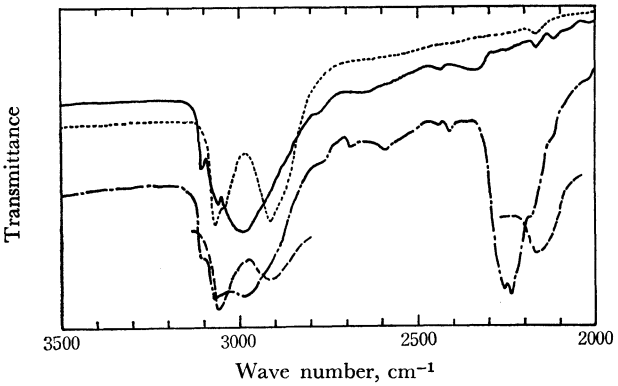


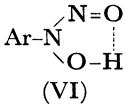
Fig. 6. IR spectra of Hcupf and deuterated Hcupf. ——; Hcupf with Nujol mull, ------; Hcupf in CCl_4, ·—·—; deuterated Hcupf with HCB mull, ----; deuterated Hcupf in CCl_4.

Table 5. The IR bands related to hydrogen bonding for Hcupf, deuterated Hcupf, and Hncupf

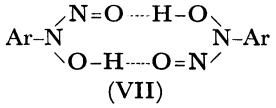
	ν(OX)		νN=O		δ(OX)		ν(N–O)		γ(OX)	
	A	B	A	B	A	B	A	B	A	B
Hcupf	2990	2915	1468	1467	1397	1388	922	921	713 742	705
Deuterated Hcupf	2240 2260	2160	1463	1467	1030	1049	873	870	531 548	528[c]
Hncupf	2910	2900[c]	1450	1448			911	912	684	703

a) X=H or D, b) A=solid, B=solution in CCl_4, c) Solution in CS_2.

cm^{-1} (solid), which corresponds to the 2980 cm^{-1} band of Hcupf, shifts to a frequency lower by only 10 cm^{-1} in CS_2 solution. The free OH stretching band was not found for either Hcupf or Hncupf not only in non-polar solvents, such as CCl_4 and CS_2, but also in proton donor solvents, such as $CHCl_3$ and $CHBr_3$. Since no change was ever observed with the bands related to the substituent in the proton-donor solvents, these compounds are considered not to form hydrogen bonding with solvents. Besides, the ν_{OH} bands are observed at relatively lower frequencies (2980 cm^{-1} for Hcupf), and the strong broad band of γ_{OH} mode is found at relatively higher frequencies (730 cm^{-1} for Hcupf and 685 cm^{-1} for Hncupf), so it is reasonable to conclude that Hcupf and Hncupf form a considerably strong hydrogen bonding, as is also to be expected on the basis of UV spectra and from the solvent effect upon the IR spectra in the frequency region lower than 1700 cm^{-1}. At present it is impossible to determine whether the hydrogen bonding is an intra-molecular type (VI) or an inter-molecular association type (VII), but the bimolecular type is considered to be more reasonable, as the stronger hydrogen bonding is sterically favored.



(VI)



(VII)

The absorption bands related to hydrogen bonding for Hcupf, deuterated Hcupf, and Hncupf are summarized in Table 5.