

Preparation and molecular configurations of some salts of dipicrylamine with organic and inorganic cations

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Abstract. An investigation has been made on the structural characteristics of a class of salts of dipicrylamine with organic and inorganic cations. A general conclusion regarding the mechanism of salt formation, nature of bondings and molecular configurations of this class of salts has been suggested from the studies on infrared spectra of these salts. The main features of the spectra of all the salts are almost similar showing similar nature of bondings and molecular configurations for all the salts. In this class of salts either organic or inorganic cations are linked with dipicrylamine anion by van der Waals forces through oxygens of one of the nitro groups of the dipicrylamine. The nitro groups are twisted out of plane of the benzene rings.

Keywords. Molecular configuration ; infrared spectra ; cholinium salt with dipicrylamine ; acetylcholinium salt with dipicrylamine ; trimethylammonium salt with dipicrylamine.

1. Introduction

Dipicrylamine i.e., 2, 4, 6-2', 4', 6'-hexanitro diphenylamine is an organic analytical reagent which due to its acidic character, on treatment with sodium, ammonium, calcium and magnesium hydroxides forms corresponding soluble salts. Kertes (1956) was the first to investigate that dipicrylamine can react with organic bases like alkylamines, pyridine, piperidine etc. and studied the possibility of methods for colorimetric estimation of these organic bases. An investigation on the salt formation of dipicrylamine with organic and inorganic bases has been carried out in this laboratory and the method has been successfully utilized in the gravimetric estimation of the organic and inorganic bases in presence of common contaminants. The mechanism of salt formation and the structural details of these salts were not known. The structural characteristics of guanidinium (Ghosh *et al* 1969) and pyridinium (Kapoor *et al* 1972) salts with dipicrylamine have already been reported. In the present discourse the structural characteristics and the molecular configurations of some other salts of dipicrylamine with organic bases viz., choline, acetyl choline, trimethylamine and some with inorganic cations

viz., K, Rb, Mg and Cs have been investigated from the studies on vibrational spectra of these salts in order to arrive at a basic understanding regarding the mode of salt formation of dipicrylamine with organic and inorganic bases.

2. Experimental

2.1. Preparation of the salts

To prepare the salts, first mexan (magnesium salt with dipicrylamine) was prepared by treating a mixture of magnesium oxide and dipicrylamine in the ratio 0.416 : 1 (by weight) in a given quantity of water with constant stirring and the precipitate (mexan) thus obtained was used as reagent for other salts of dipicrylamine due to its higher solubility in water compared to that of dipicrylamine.

The cholinium, acetylcholinium and trimethylammonium salts with dipicrylamine were prepared by adding dropwise the aqueous solution of the respective chloride salts in 3% aqueous solution of mexan with constant stirring at room temperature (28–30°C). The reactions were instantaneous giving red crystalline precipitates of the cholinium, acetylcholinium and trimethylammonium salts with dipicrylamine. The precipitates were washed with ice cold distilled water and dried to constant weight at 100°C. In the case of trimethylammonium salt, the trimethylammonium chloride was first prepared by neutralizing an aqueous solution of trimethylamine (40% wt/vol) with requisite amount of *N*/10 hydrochloric acid using methyl red as indicator. The neutral aqueous solution of trimethylammonium chloride was allowed to concentrate on a water bath to obtain crystalline mass of trimethylammonium chloride.

Potassium, rubidium and cesium salts with dipicrylamine were prepared by reacting the respective chloride salts with mexan. The precipitates of the respective salts were washed with saturated solutions of the salts to make the precipitates free from mexan, if any, and dried at room temperature. The chemical composition of the products are shown in table 1.

2.2. Apparatus

2.2a. *Infrared spectra* : The infrared spectra of the salts along with the parent materials were recorded on a Perkin Elmer 421-model dual grating infrared spectrophotometer in the frequency range from 4000 to 550 cm^{-1} using a scanning speed of 17 min for the entire range. The pure and crystallised samples were subjected to infrared recording in KBr matrix. About 2 mg of the samples were mixed thoroughly with 250–300 mg KBr powder. The mixture was placed in a stainless steel vacuum die and pressed under hydraulic press for 10 min at 15 tons/sq. inch pressure. The pellets of dimension 13 mm thus formed were subjected to infrared studies.

2.2b. *Dipole moment* : The dipole moments of dipicrylamine and potassium salt with dipicrylamine were measured by the principle of heterodyne beat method in a dipole meter (WTW, Germany) with the accuracy of order 10^{-4} . Measurements were done at a frequency of 1 Mc/sec. and at 30°C in benzene solution of weight fraction not exceeding 0.05. Halverstadt-Kumlers method (Halverstadt *et al* 1942) was applied to calculate the dipole moment values.

Table 1. Chemical composition of the resulting salts

Resulting salt	% Carbon		% Hydrogen		% Nitrogen		% Oxygen		% Metal	
	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
Cholinium salt with dipicrylamine (C ₂ H ₄ NO) ⁺ (C ₁₂ H ₄ N ₇ O ₁₂) ⁻	37.67	37.65	3.47	3.35	20.40	20.66	38.30	38.35		
Acetyl cholinium salt with dipicrylamine (C ₇ H ₁₆ NO ₂) ⁺ (C ₁₂ H ₄ N ₇ O ₁₂) ⁻	38.80	39.05	3.40	3.45	19.30	19.17	38.10	38.33		
Trimethyl ammonium salt with dipicryl- amine (C ₃ H ₁₀ N) ⁺ (C ₁₂ H ₄ N ₇ O ₁₂) ⁻	35.95	36.15	2.85	2.83	22.60	22.49	38.40	38.53		
Magnesium salt with dipicrylamine Mg ⁺ (C ₁₂ H ₄ N ₇ O ₁₂) ⁻	31.30	31.16	0.870	0.872	21.10	21.20	41.40	41.51	5.22	5.26
Potassium salt with dipicrylamine K ⁺ (C ₁₂ H ₄ N ₇ O ₁₂) ⁻	30.30	30.20	0.815	0.845	20.60	20.54	40.00	40.22	8.15	8.19
Rubidium salt with dipicrylamine Rb ⁺ (C ₁₂ H ₄ N ₇ O ₁₂) ⁻	27.48	27.52	0.765	0.770	18.85	18.72	36.55	36.66	16.28	16.32
Cesium salt with dipicrylamine Cs ⁺ (C ₁₂ H ₄ N ₇ O ₁₂) ⁻	25.00	25.24	0.701	0.706	17.17	17.17	33.80	33.62	23.20	23.37

3. Results and discussions

The infrared spectra of all the resulting salts are almost similar. The representative spectra of one salt with organic cation (viz., cholinium salt) along with its parent materials are shown in figure 1 and the spectra of the salts with inorganic cations are shown in figure 2. The important absorption frequencies which have been affected on salt formation are listed in table 2.

The main features of infrared spectra of all the resulting salts being similar, it is expected that the nature of bonding, mode of salt formation and the molecular configurations will be same for all the salts. So, the structural characteristics with respect to cholinium salt with dipicrylamine have been discussed in detail.

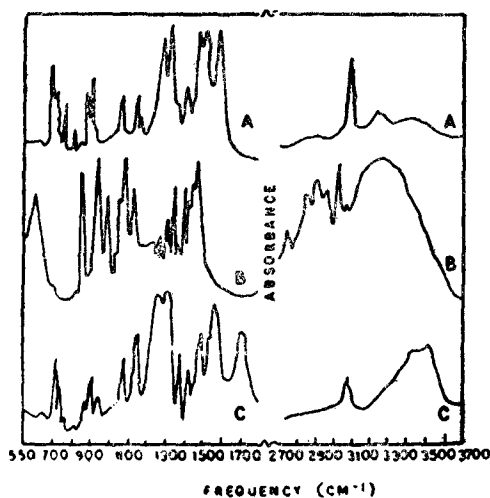


Figure 1. Infrared spectra of (A) Dipicrylamine, (B) Cholinium chloride, (C) Cholinium salt with dipicrylamine.

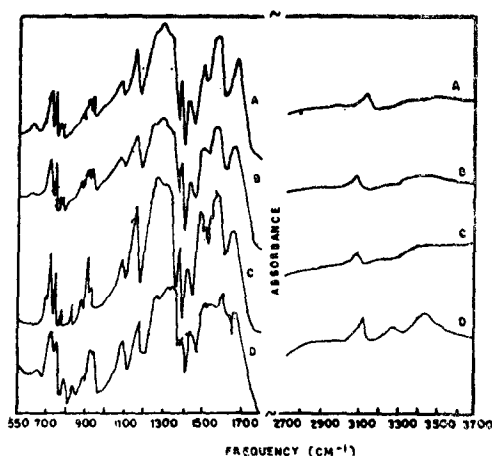


Figure 2. Infrared spectra of (A) Potassium salt with dipicrylamine, (B) Rubidium salt with dipicrylamine, (C) Cesium salt with dipicrylamine, (D) Magnesium salt with dipicrylamine.

Table 2. Important absorption frequencies with assignments

Name of the compounds	Absorption frequency (cm ⁻¹) due to							
	NH stretching	Phenyl (C=C skeletal in plane)	C = N stretching (Ph—N = Ph)	C—NO ₂ asymmetrical stretching	C—NO ₂ symmetrical stretching	NH deformation in plane	CH ₂ -N asymmetrical bending	CH ₃ -N symmetrical bending
1. Dipicrylamine	3245 ms,br	1655 w,sh 1623 m,sh 1602 vs,sp		1530 vs	1345 vs	1505 m		
2. Cholinium chloride			1720 s	1565 vs	1333 sh		1472 s	1403 ms
3. Acetyl cholinium chloride			1740 s,br	1567 vs			1480 vs	1410 ms
4. Trimethylammonium chloride							1475 vs	1401 ms
5. Cholinium salt with dipicrylamine							1473 sh	1376 s
6. Acetylcholinium salt with dipicrylamine			1722 s	1562 vs	1335 sh		1475 w,sh	1380 ms
7. Trimethylammonium salt with dipicrylamine							1473 m,sh	1378 ms
8. Potassium salt with dipicrylamine			1665 vs	1565 s	1338 sh			
9. Rubidium salt with dipicrylamine			1665 vs	1570 s	1338 sh			
10. Cesium salt with dipicrylamine			1665 vs	1570 s	1338 sh			
11. Magnesium salt with dipicrylamine			1670 vs	1560 w	1338 sh			

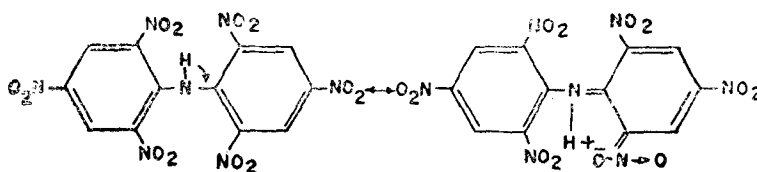


Figure 3. Resonating structures of dipicrylamine.

It may be mentioned here that dipicrylamine has a number of resonating forms of which two forms contribute predominantly to the resonance as shown in figure 3. Comparing the occurrence of absorption bands in diphenylamine and related compounds (Bellamy and Beecher 1952 ; Bellamy 1958 ; Hadzi and Skrbizak 1957) in the region $1655\text{-}1600\text{ cm}^{-1}$, it appears that the band at $1720\text{-}1740\text{ cm}^{-1}$ region in the case of organic salts and at $1670\text{-}1665\text{ cm}^{-1}$ in the case of inorganic salts is too high in frequency to be assigned to aromatic ring vibration only. However, in the type of compounds having structural element $\text{Ph}-\text{N}=\text{Ph}$ which of course, contains $\text{C}=\text{N}$ link, a strong band at higher frequency around 1670 cm^{-1} has been observed by Marion *et al* (1951) and this is the characteristic of anilino structures, in general, and indolenines in particular. Accordingly, it is reasonable to assign the band at $1720\text{-}1740\text{ cm}^{-1}$ region to $\text{C}=\text{N}$ vibration coupled with aromatic ring vibration ($\text{Ph}-\text{N}=\text{Ph}$). This band has consistently appeared in other salts of dipicrylamine and this bonding is also in conformity with the structure of guanidinium (Gupta and Datta 1975) and potassium (Kundu and Ghosh 1980) salts with dipicrylamine determined by x-ray method. Further, the N-H deformation mode (Rud'Co *et al* 1969) which has appeared at 1505 cm^{-1} in the spectrum of dipicrylamine is absent in the spectra of the salts. These suggest that cholinium chloride reacts with resonating form (II) of the dipicrylamine in preference to that with other resonating form (I) (figure 3). This is also supported by the faster rate of reaction of cholinium chloride with dipicrylamine to form the cholinium salt with dipicrylamine. Since the reaction rate of both types of salt (organic and inorganic) is similar, it may be assumed that the band due to structural element $\text{Ph}-\text{N}=\text{Ph}$ for both types of salts appear in the region mentioned above.

The band at 1530 cm^{-1} as observed in the spectrum of dipicrylamine conforms to the normal asymmetrical $\text{C}-\text{NO}_2$ stretching vibration (Bellamy 1958). In the spectra of the salts the strong band in the region $1565\text{-}1555\text{ cm}^{-1}$ may be presumed to be the displaced frequency of the nitro groups which are twisted out of plane of the aromatic rings due to the steric effect and also due to the presence of choline ion in the vicinity of the nitro groups which take part in the salt formation by van der Waals forces. The displacement of nitro groups to higher frequency due to the presence of a strong electronegative group in the para position or of a large group in the ortho position have been stated in the literature (Conduit 1959). The same phenomenon has been observed in the structure of guanidinium salt with dipicrylamine. Similar is the case with the symmetrical vibration which has been shifted from 1345 cm^{-1} to $1338\text{-}1333\text{ cm}^{-1}$ region.

The asymmetrical and symmetrical vibration frequencies of $\text{C}-\text{NO}_2$ of dipicrylamine due to salt formation with inorganic cations also change in a similar

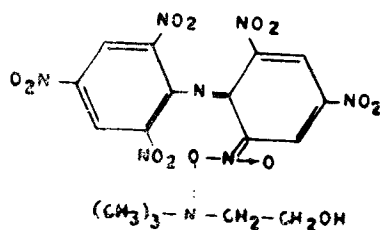


Figure 4. Possible molecular configuration of cholinium salt with dipicrylamine.

way as in the case of organic salts. In the structure of rubidium hydrogen di-*o*-nitrobenzoate and potassium hydrogen di-*p*-nitrobenzoate, Shrivastava and Speakman (1961) have shown that nitro groups are twisted out of plane of the benzene rings due to the linkage of metal ions with oxygen of NO_2 group. Banerjee *et al* (1969) have also shown that in the case of alkali metal complex with *o*-nitrobenzoic acid, $\text{N}=\text{O}$ frequency is metal sensitive. The twisting of the NO_2 groups out of plane of the aromatic rings due to the linkage like $\text{K} \cdots \text{ONO}$ is further confirmed from the crystal structure of the potassium salt with dipicrylamine. Again, the symmetrical deformation mode ($\text{CH}_3\text{-N}$) at $1410\text{-}1400\text{ cm}^{-1}$ of cholinium chloride is shifted in the salt, there is a decrease in the intensity of the asymmetrical deformation mode around 1472 cm^{-1} and enhancement of the intensity of the absorption band in the region $1380\text{-}1375\text{ cm}^{-1}$ due to the salt formation. The enhancement of intensity is probably due to overlapping of $\text{CH}_3\text{-N}$ symmetrical deformation mode in the region $1410\text{-}1400\text{ cm}^{-1}$ which has been lowered at $1380\text{-}1375\text{ cm}^{-1}$ due to the salt formation, since the absorption band at $1410\text{-}1400\text{ cm}^{-1}$ is absent in the spectra of the resulting salt. The same phenomena have been observed in the case of acetyl cholinium and trimethylammonium salts with dipicrylamine. The possible molecular configuration of the cholinium salt with dipicrylamine is as shown in figure 4.

4. Conclusion

Dipicrylamine exists in resonating forms involving structural elements, Ph-N-Ph and Ph-N=Ph which are not equivalent. When dipicrylamine reacts with organic and inorganic bases, the first resonating form is restricted and second resonating form takes part in the reaction to form the respective salts. In the structure of the salts of dipicrylamine, resonance occurs between the structures involving structural element Ph-N=Ph and Ph=N-Ph , which are equivalent. The presence of dipole moment in dipicrylamine (3.68×10^{-18} esu) and in the potassium salt (4.96×10^{-18} esu) also indicates that both structures are resonating in character which is further confirmed from the structure of the potassium salt (Kundu and Ghosh 1980). In the potassium salt the dipole moment is lowered because of less resonance energy compared to that of dipicrylamine. This suggests that the potassium salt has equivalent resonating structures while dipicrylamine has non-equivalent resonating structures (Pauling 1960).

It may therefore be concluded that dipicrylamine forms salts with both organic and inorganic cations in similar fashion. The nature of bondings and linkage

of dipicrylamine anions with organic and inorganic cations are same in both types of salts although the individual crystal structures may be different. Ghosh *et al* (1968) have shown that when potassium nitrate reacts with the guanidinium salt with dipicrylamine in water, potassium can replace guanidine ion forming the potassium salt with dipicrylamine. The exchangeability of organic ion by inorganic ion also corroborates the similar molecular configurations of both types of salts of dipicrylamine. This class of salts may be regarded as a loose molecular complex type.

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