CHAPTER VIII
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SUMMARY AND CONCLUSIONS

The present study is focused on the synthesis and characterization of some biologically active carbanionic sigma complexes and donor–acceptor adducts derived from nitro aromatics such as 1-chloro-2,4-dinitrobenzene (DNCB), 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitro-1,3-benzenediol (styphnic acid).

In chapter I, various types of interactions feasible between electron-deficient nitro aromatics and bases are described. Different types of carbon-bonded sigma complexes, their characterization and significance of donor-acceptor adducts are also documented.

In chapter II, aim and scope of the present investigation is enlightened.

Purification of reagents, synthesis of carbon-bonded sigma complexes and donor-acceptor adducts and screening methods adopted to examine biological activity of the synthesized molecules are presented in chapter III.

In chapter IV, characterization of two extraordinarily stable carbanionic sigma complexes (barbiturates) – (i) triethylammonium 2,4-dinitrophenylbarbiturate [systematic name – triethylammonium 5-(2,4-dinitrophenyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate)] obtained from DNCB, pyrimidine – 2,4,6(1H, 3H, 5H)-trione (barbituric acid) and triethylamine and (ii) tri-n-butylammonium 2,4-dinitrophenylbarbiturate [systematic name – tri-n-butylammonium 5-(2,4-dinitrophenyl -2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate)] prepared from DNCB, barbituric acid and tri-n-butylamine is discussed. These two barbiturates are water soluble and show significant anticonvulsant / hypnotic activity. Acute toxicity studies, carried out with the synthesized barbiturates, reveal that LD₅₀ of barbiturate (i) is greater than 1000 mg/kg and that of (ii) is greater than 490 mg/kg. The animals have not shown any sign of acute toxicity and behavioural changes. The synthesized barbiturates of the present investigation may probably potent drugs in future for grand mal type of
convulsion because of their extraordinary stability, low toxicity, high solubility in water and easy method of preparation.

In chapter V, a novel reaction which occurs between DNCB and β-ketoesters (ethyl, methyl and tert-butyl acetoacetate) in the presence of triethylamine is highlighted. The reaction involves carbanionic sigma complex intermediate. The ultimate product has been identified as alkyl 2,2-bis(2,4-dinitrophenyl)ethanone (alkyl group: ethyl, methyl, tert-butyl). The product has four nitro groups and high density and hence thermal characterization such as impact sensitivity test and TG/DTA analysis are also carried out. Thermal characterization implies that the tetra nitro compounds are insensitive secondary explosives. The novel one-pot synthesis of the present investigation for the preparation of high energy alkyl 2,2-bis(2,4-dinitrophenyl)ethanoates through the formation of carbanionic sigma complex intermediate may gain importance in future due to (i) the synthetic method involves ethanol as solvent which poses less environmental pollution than other organic solvents and (ii) the products are obtained in good yield (70 – 80%) with high purity. The products also show moderate antimicrobial activity.

In chapter VI, the conformational aspect of the two rings of the bicyclic adducts of the carbanionic sigma complexes derived from 1,3,5-trinitrobenzene and ethyl 2-benzyl-3-oxobutanoate / ethyl 2(4-nitrophenylmethyl)-3-oxobutanonate in the presence of triethylamine is illustrated. Upon recrystallisation, the bicyclic adducts — i) triethylammonium 2-benzyl-2-ethoxycarbonyl-3-oxo-8,9-dinitro-bicyclo[3.3.1]non-7-en-6-nitronate and ii) triethylammonium 2(4-nitrophenylmethyl)-2-ethoxycarbonyl-3-oxo-8,9-dinitro-bicyclo[3.3.1]non-7-en-6-nitronate are obtained in good crystalline form with extraordinary stability. The crystal blocks are subjected for single crystal X-ray analysis. From the puckering parameter values, chair-envelop conformation has been assigned to the rings of bicyclic adducts. The bicyclic adducts exhibit moderate antimicrobial activity. This piece of work may help to modify the conformation of the rings by suitably placing the substituents in the two rings to enhance the biological activity of the bicyclic adducts.
The types of interactions between styphnic acid and bases [tetrahydro-1,4-oxazine (morpholine), 2-methylaniline and 2-methoxyaniline] are scrutinized and presented in chapter VII. Spectral studies imply that proton transfer from the phenolic OH of styphnic acid to the nitrogen atom of the base is the main contributing factor for the formation of the adduct. Single crystal X-ray analysis results strongly support the spectral observations. Though styphnic acid has two phenolic OH groups, it forms 1:1 adduct even at high base concentrations. The adducts prepared from styphnic acid and substituted anilines (i. 2-methylbenzenaminium 3-hydroxy-2,4,6-trinitrophenolate and ii. 2-methoxybenzenaminium 3-hydroxy-2,4,6-trinitrophenolate) are noticed to exhibit antimicrobial and wound healing activities. Besides these two activities, the adduct derived from styphnic acid and morpholine (morpholin-4-ium 3-hydroxy-2,4,6-trinitrophenolate) exhibits anticonvulsant activity also. All the isolated adducts are high density materials. These adducts may presumably be utilized in two fields (i. medicine and ii. energetics) in future.