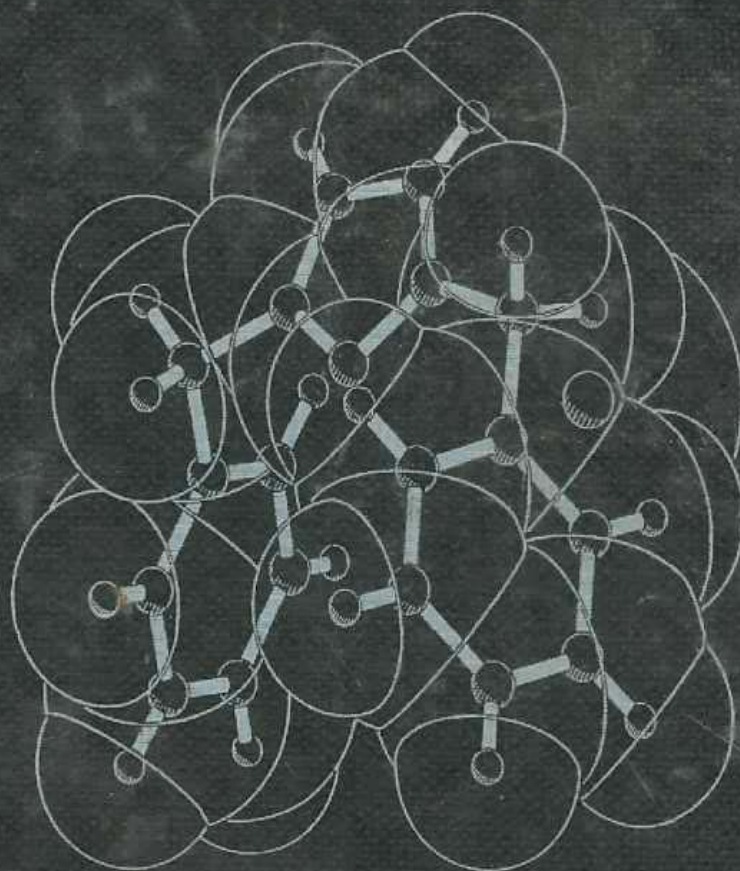


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# Crystal and Molecular Structure Studies of Some Triazoles and Mesogens

(Ph.D Thesis, 1997)



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# **Crystal and Molecular Structure Studies of Some Triazoles and Mesogens**

Thesis Submitted to the  
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for the degree of

**Doctor of Philosophy**

by

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*January 1997*

**To my Parents and Teachers**

## **DECLARATION**

I hereby declare that the present thesis has been compiled by myself independently and that it has not previously formed the basis for the award of any degree, diploma, associateship, fellowship or other similar titles.

  
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## CERTIFICATE

I certify that this thesis has been composed by Mr. Lokanath N.K, based on the investigations carried out by him at the Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore 570 006 under my supervision. The subject matter has not previously formed the basis for the award of any degree, diploma, associateship, fellowship or other similar titles.



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Finally, I thank all those who have helped directly or indirectly for the fulfillment of this thesis.

N K Lokanath

# SYNOPSIS

The thesis entitled "Crystal and Molecular Structure Studies of Some Triazoles and Mesogens" contains X-ray crystallographic details of eight nitrenium compounds and a mesogen. The text of this thesis is spread over eleven chapters and a brief description of each chapter is presented in this synopsis.

## CHAPTER I - Introduction to Materials Studied

This chapter gives a brief introduction to the nitrenium compounds, their properties and applications. This followed by the basic concepts of diffraction of X-rays by crystals, the methods of determining the unit cell parameters and the space groups, practical aspects of collecting and processing the intensity data, for overcoming the phase problem in crystallography-Patterson technique and Direct methods, and the procedures of refinement of the model structure have been reviewed.

## CHAPTER II - Crystal Structure of 1-methyl-3-phenyl-1,2,3-triazolium perchlorate

This compound ( $C_9H_{12}O_4N_3Cl$ ) crystallizes in the monoclinic spacegroup  $P2_1/c$  with  $a = 14.457(3)\text{\AA}$ ,  $b = 5.9985(3)\text{\AA}$ ,  $c = 14.543(4)\text{\AA}$  and  $\beta = 113.54(2)^\circ$ ,  $Z = 4$ . The structure was solved by direct method and refined to  $R = 0.053$ ,  $R_w = 0.050$  for 1368 reflections with  $I > 3\sigma(I)$ . The crystal structure shows that the anion  $ClO_4^-$  is not directly connected to the cationic part of the respective nitrenium ion.  $ClO_4^-$  holds cation by means of C-H.....  $ClO_4^-$  hydrogen bonds. The C-H...  $ClO_4^-$  intermolecular interaction appears to be responsible for molecular cohesion in the unit cell. The cationic part of the nitrenium ion is planar, phenyl and five-membered ring are independently planar. Packing of molecules in the unit cell show stacking of molecules in pairs when viewed down  $b$ -axis.

### CHAPTER III - Crystal Structure of 1,3-dimethyl-benzotriazolium trifluoromethane sulfonate

The title compound ( $C_9H_{10}O_3N_3F_3S$ ) crystallizes in the monoclinic spacegroup  $P2_1/c$  with  $a = 6.864(2)$  Å,  $b = 11.319(2)$  Å,  $c = 16.557(3)$  Å and  $\beta = 91.25(2)^\circ$ ,  $Z = 4$ . The structure was solved by direct method and refined to  $R = 0.062$ ,  $R_w = 0.087$  for 1336 reflections with  $I > 3\sigma(I)$ . The crystal structure shows that the anion  $CF_3SO_3^-$  is not directly connected to the cationic part of the respective nitrenium ion.  $CF_3SO_3^-$  holds cation by means of C-H...  $CF_3SO_3^-$  hydrogen bonds. The C-H...  $CF_3SO_3^-$  intermolecular interaction appears to be responsible for molecular cohesion in the unit cell. Phenyl and five-membered ring are independently planar. The cation part of the nitrenium compound is also planar. Packing of molecules in the unit cell shows stacking of molecules when viewed down  $a$ -axis.

### CHAPTER IV - Crystal Structure of 1,3-dibenzyl-triazolium-iodide

The title compound ( $C_{32}H_{35}N_6I_2$ ) crystallizes in the primitive monoclinic spacegroup  $P2_1/c$   $a = 9.895(5)$  Å,  $b = 11.041(3)$  Å,  $c = 29.475(9)$  Å and  $\beta = 92.44(4)^\circ$ ,  $Z = 4$ . The structure was solved by direct method and refined to  $R = 0.030$ ,  $R_w = 0.037$  for 2478 reflections with  $I > 3\sigma(I)$ . The crystal structure shows that the anion  $I^-$  is not directly connected to the cationic part of the respective nitrenium ion in both molecules in the asymmetric unit.  $I^-$  holds cation by means of C-H... $I^-$  hydrogen bonds. All the phenyl rings and five-membered rings are independently planar in both the molecules of the asymmetric unit. The N — N — N bond angle and bond distances of the five-membered ring are of interest. Packing of molecules in the unit cell show no herring bone is observed when viewed down  $a$ -axis. Comparing the dihedral angle between the corresponding rings in molecule 1 and molecule 2 of the asymmetric unit shows slightly different conformation.

### CHAPTER V - Crystal Structure of 4-phenyl imidazole

4-phenyl imidazole, ( $C_{18}H_{16}N_4$ ), an intermediate compound, crystallizes in the primitive monoclinic space group  $pa$  with dimensions,  $a = 7.029(1) \text{ \AA}$ ,  $b = 12.5142(8) \text{ \AA}$ ,  $c = 9.448(1) \text{ \AA}$ ,  $\beta = 100.64(1)^\circ$ ,  $Z = 2$ . The structure was solved by direct methods(SIR92) and refined to  $R = 0.032$ ,  $R_w = 0.036$  using 1220 reflections with  $I > 3\sigma(I)$ . Molecules in the unit cell are stacked in pairs when viewed down c-axis. Two molecules in the asymmetric unit shows no variation of bond lengths and angles. Phenyl and five membered rings are independently planar in both the molecules of the asymmetric unit. Comparing the dihedral angle between the corresponding rings in molecule 1 and molecule 2 of the asymmetric unit shows slightly different conformation.

### CHAPTER VI - Crystal structure of 1-benzyl-4-phenyl-1,2,3-triazole

This compound ( $C_9H_9N_3$ ) crystallizes in primitive monoclinic spacegroup  $P2_1$  with  $a = 5.545(6) \text{ \AA}$ ,  $b = 7.777(2) \text{ \AA}$ ,  $c = 9.850(4) \text{ \AA}$ ,  $\beta = 96.36(5)^\circ$ ,  $Z = 2$ . The structure was solved by direct methods(SIR92) and refined to  $R = 0.047$ ,  $R_w = 0.070$  for 756 reflections with  $I > 3\sigma(I)$ . Phenyl and five membered rings are independently planar. The stacking of molecules one above another when viewed down a-axis.

### CHAPTER VII - Crystal Structure of 3,5-diphenyl triazole

This compound ( $C_{14}H_{11}N_3$ ) crystallizes in the C-centered monoclinic space group  $Cc$  with  $a = 26.982(6) \text{ \AA}$ ,  $b = 5.681(4) \text{ \AA}$ ,  $c = 7.439(2) \text{ \AA}$ ,  $\beta = 103.54^\circ$ ,  $Z = 4$ . The structure was solved by direct methods(SIR92) and refined to  $R = 0.033$ ,  $R_w = 0.040$  for 856 reflections with  $I > 3\sigma(I)$ . Packing of molecules in the unit cell down a-axis shows stacking of molecules in pairs. Phenyl rings and five-membered ring are independently planar.

### CHAPTER VIII - Crystal Structure of 1-benzyl-4-phenyl-1,2,3-triazole

The title compound ( $C_{15}H_{13}N_3$ ) crystallizes in the primitive monoclinic space group  $P2_1/c$  with dimensions  $a = 6.038(2)$  Å,  $b = 8.094(3)$  Å,  $c = 25.62(1)$  Å,  $\beta = 93.80(4)^\circ$ ,  $Z = 4$ . The structure was solved by direct method and refined to  $R = 0.074$ ,  $R_w = 0.085$  for 1644 reflections with  $I > 3.00\sigma(I)$ . Two phenyl rings and five-membered rings are independently planar.

### CHAPTER IX - Crystal Structure of N-benzyl N-phenyl benzamide

The title compound ( $C_{20}H_{17}NO$ ) crystallizes in the C-centered monoclinic space group  $C2/c$  with dimensions  $a = 25.433(4)$  Å,  $b = 9.176(4)$  Å,  $c = 16.711(4)$  Å,  $\beta = 125.89(1)^\circ$ ,  $Z = 8$ . The structure was solved by direct methods(SIR92) and refined to  $R = 0.035$ ,  $R_w = 0.036$  using 1524 reflections with  $I > 3.00\sigma(I)$ . The molecular structure is stabilized by intramolecular hydrogen bonds of the C-H....O and C-H....N. All the phenyl rings are independently planar. Packing of molecules in the unit cell projected down  $a$ -axis shows stacking of molecules in pairs.

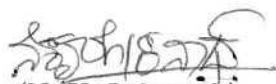
### CHAPTER X - Crystal Structure of an Interesting Nematogen

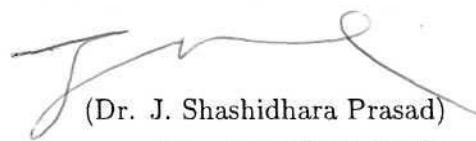
This chapter gives brief introduction to liquid crystal followed by crystal structure of Di-(2,7-disubstituted-9-fluorenyl) glutamate. The nematic compound ( $C_{83}H_{84}O_{12}$ ) crystallizes in primitive triclinic space group  $P\bar{1}$  with dimensions  $a = 16.173(5)$  Å,  $b = 16.233(5)$  Å,  $c = 14.320(5)$  Å,  $\alpha = 91.124(5)^\circ$ ,  $\beta = 105.098(5)^\circ$ ,  $\gamma = 92.270(5)^\circ$ ,  $Z = 2$ . The structure was solved by direct methods(SHELXS-86) and refined to  $R1 = 0.097$ ,  $wR2 = 0.280$  using 9682 reflections with  $I > 2\sigma(I)$ . Disorder is found in few atoms due to the larger thermal motion or disorder, as indicated by the large and highly anisotropic temperature factors. Packing of molecules in the unit cell show strong im-

brication as expected for a nematic mesogen. The bond distances and angles are in good agreement with other mesogenic materials. The torsion angles of the end chains shows that the end chains assume extended conformation. All the phenyl rings are independently planar. The molecular structure is stabilized by intramolecular hydrogen bonds of the type C - H .....O.

### **CHAPTER XI - Structure Property Relationship**

This chapter summarizes the important results from the structural studies of nitrenium compounds and a mesogen. The bond angles and bond distances of the five-membered ring of the nitrenium compounds were compared with the reported structures.

  
(N. K. Lokanath)  
Signature of the Fellow

  
(Dr. J. Shashidhara Prasad)  
Signature of the Guide

**List of publications**

1. Crystal structure of 1-benzyl-1,2,3-triazole: Sridhar M.A, Lokanath N.K, Shashidhara Prasad J, Bhadre Gowda D.G, Rangappa K.S, *Z. Kristallogr.*, 1996 (accepted).
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3. Crystal structure of 1-benzyl-4-phenyl-1,2,3-triazole: Lokanath N.K, Sridhar M.A, Shashidhara Prasad J, Bhadre Gowda D.G, Rangappa K.S, *Z. Kristallogr.*, 1996 (accepted).
4. Crystal Structure of 1,3-Dibenzyl-triazolium-iodide: Lokanath N.K, Sridhar M.A, Shashidhara Prasad J, Gernot Boche, Rangappa K.S, *Z. Kristallogr.*, 1996 (communicated).
5. Crystal Structure of 4-phenyl imidazole: Lokanath N.K, Sridhar M.A, Shashidhara Prasad J, Gernot Boche, Rangappa K.S, *Z. Kristallogr.*, 1996 (communicated).
6. Crystal Structure of 1,3-dimethyl-benzotriazolium trifluoromethane sulfonate: Lokanath N.K, Sridhar M.A, Shashidhara Prasad J, Gernot Boche, Rangappa K.S, *Z. Kristallogr.*, 1996 (communicated).
7. Crystal Structure of 3,5-dibenzyl-triazole: Lokanath N.K, Sridhar M.A, Shashidhara Prasad J, Gernot Boche, Rangappa K.S, *Z. Kristallogr.*, 1996 (communicated).
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15. Crystal structure of 4-isothiocyanatophenyl 4-pentylbicyclo [2,2,2] octane-1-carboxylate: Sridhar M.A, Lokanath N.K, Revannasiddaiah D, Shashidhara Prasad J, *Mol. Cryst. Liq. Cryst.*, 1996 (accepted).
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26. Crystal and Molecular structure studies of some organic haloamines : Lokanath N.K, Yathirajan H.S, Sridhar M.A, Shashidhara Prasad J, *Inorg.chem.(J. Am.Chem.Soc)*, 1997 (communicated).

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