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An Insight in to the Crystallographic Aspects of Quinolines

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Abstract—*In this paper, an attempt has been made to carry out a crystallographic comparison of some geometrical and structural features for a series of quinoline derivatives of alkaloids. Selected bond distances and bond angles of interest in a series of quinoline derivatives have been discussed in detail, besides conformations of ring systems, their graphical presentation and their frequency of occurrence. An overview of crystal structure analysis with emphasis on the role of hydrogen bonding in some quinoline derivatives (alkaloids) is presented in this paper. The role of hydrogen bonding in quinoline derivatives has been found to be predominant and this observation makes the role of hydrogen bonding in these organic molecular assemblies very important.*

1. INTRODUCTION

Alkaloids are a group of naturally occurring chemical compounds that mostly contain basic nitrogen atoms. Alkaloid containing plants have been used by humans since ancient times for therapeutic and recreational purposes. Compared with most other classes of natural product, alkaloids are characterized by great structural diversity and there is no uniform classification scheme for alkaloids. Quinoline is a heterocyclic aromatic organic compound with the chemical formula C_9H_7N (Figure 1). It is a colorless hygroscopic liquid with a strong odor. Aged samples, especially if exposed to light, become yellow and later brown. Quinoline is slightly soluble in cold water but dissolves readily in hot water and most organic solvents. Quinoline itself has few applications, but many of its derivatives are useful in diverse applications. A prominent example is quinine, an alkaloid found in plants. 4-Hydroxy-2-alkylquinolines (HAQs) are involved in antibiotic resistance. The term includes the more specific "antibiotic resistance", which applies only to bacteria becoming resistant to antibiotics. Resistant microbes are more difficult to treat, requiring alternative medications or higher doses, both of which may be more expensive or more toxic. Microbes resistant to multiple antimicrobials are called multidrug resistant (MDR); or sometimes superbugs [1]. Quinolines are found in natural products [2] numerous commercial products including fragrances, dyes [3] and biologically active compounds [4-5] and exhibit diverse range of pharmacological activities such as anti-viral, anti-cancer, anti-bacterial, anti-fungal, anti-inflammatory [6-9]. Among quinoline derivatives, tetrahydroquinolines (THQs) are important structural subunits of natural and synthetic products and many THQ derivatives exhibit interesting biological and pharmacological activities like anti-malarial [10] cholesteryl ester transfer protein inhibitors [11] anti-diabetic [12].

The present work provides comprehensive information about structural features and packing interactions/hydrogen bonding in quinoline derivatives. Here, we have identified a series of twenty-five derivatives of quinoline from the literature (CSD). The reference code, chemical name, chemical formula, molecular weight and published reference [13-35] of each molecule is presented in Table 1.

2. RESULTS AND DISCUSSION

2.1. Comparative Geometrical Parameters

2.1.1. Crystallization

All the molecules crystallized by slow evaporation. It is a solution technique essentially used for the growth of single crystals of organic molecules through the process of evaporation.

2.1.2. Bond distances and angles

Most of the molecules undertaken contain substitutional groups at C2 and C7 positions. Therefore, it is of interest to investigate N1-C2, C2-C3, C6-C7 and C7-C8 bond distances and N1-C2-C3 and C6-C7-C8 bond angles and their data is presented in Table 2 and 3.

The substitution of groups at C2 and C7 positions of the quinolinal nucleus causes significant change in the value of bond distances in rings A and B, depending upon whether N1-C2, C2-C3, C6-C7 and C7-C8 is a single or double bond. The bond distance N1(sp^3)-C2(sp^2) lies in the range 1.378-1.408 Å[average value of 1.386Å]. The bond distance N1(sp^3)-C2(sp^2) in molecule 11(1.378 Å), 15(1.379 Å), 17(1.379 Å), 18(1.379 Å) and 19(1.377 Å) is shorter than the standard value of 1.383Å [36]. The bond distance C2(sp^2)-C3(sp^2) lies in the range 1.334-1.368 Å[average value of 1.354Å]. The said bond distance in molecule 5(1.347 Å), 7(1.346 Å), 21(1.334 Å) and

25(1.349 Å) shows a significant deviation from accepted value of 1.353 Å. The deviation of bond distances N1(sp^3)-C2(sp^2) and C2(sp^2)-C3(sp^2) could be due to the effect of some functional group located at C2 position which invariably is involved in C-H…O intra/intermolecular interactions.

The bond distance C7(sp^3)-C8(sp^3) lies in the range 1.46-1.56 Å [average value of 1.52Å]. The said bond distance in molecule 4(1.46 Å) shows a significant deviation from accepted value of 1.53Å The bond distance C6(sp^3)-C7(sp^3) lies in the range 1.44-1.57 Å[average value of 1.53Å]. The said bond distance in molecule 4(1.44 Å) shows a significant deviation from accepted value of 1.53Å [36].The deviation of bond distances C6(sp^3)-C2(sp^3) and C7(sp^3)-C8(sp^3) could be due to the effect of some functional group located at C7 position.

The substitution of a group at C2 position also causes a significant change in the value of bond angle N1-C2-C3 in ring A. The bond angle N1-C2-C3 in molecules with a substituent group at the C2(sp^2) position varies from 116.5° to 120.5° [average value of 119.8°]. The said bond angles in molecule 4(116.5°) and 21(120.4°) shows a significant deviation from average value of 119.8°, which may be due to the effect of some functional group located at C2 position which invariably is involved in C-H…O/N-H…O intra/intermolecular interactions.

The substitution of a group at C7 position also causes a significant change in the value of bond angle C6-C7-C8 in ring B. The bond angle C6-C7-C8 in molecules with a substituent group at the C7(sp^3) position varies from 106.5° to 116.8° [average value of 109.3°]. The said bond angles in molecule 1(116.2°), 2(112.5°), 3(113.4°) and 4(116.8°) shows a significant deviation from average value of 109.3°, which may be due to the effect of some functional group located at C7 position which invariably is involved in C-H…O/N-H…O intermolecular interactions.

2.1.3. Ring conformations and their graphical representations

Asymmetry parameters (ΔC_2 and ΔC_s) play an important role in describing the conformation of six-membered quinoline moiety of compounds. The asymmetry parameters have been calculated for the individual ring systems of all the molecules (1-25) and their detailed analysis shows the existence of different types of conformations. These conformations as obtained for individual ring system of quinoline moiety are presented in Table 4. The following observations can be made from the different ring conformations as adopted by individual ring A and B of molecules (1-25). The incidence of occurrence of a boat conformation in ring A is quite large (32%) followed by sofa (24%), flat boat (12%), shallow boat & half chair (8%) and half boat, screw boat, distorted boat, pseudo boat (4%), respectively (Figure 2a). In ring B, the incidence of occurrence of an envelope conformation is quite large (36%) followed by sofa (28%), half chair (20%), intermediate between sofa and half chair (8%) and intermediate between envelope and half chair & half boat (4%), respectively (Figure 2b).

2.1.4. Hydrogen bonding

The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X-H in which X is more electronegative than H and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation [37]. Pauling in 1939, explained hydrogen bonding in his book *The Nature of the Chemical Bond* [38]. Strong and weak hydrogen bonds are discussed by Jeffrey and Saenger, in *Hydrogen Bonding in Biological Structures* [39].

Based on comparative data of intra- and intermolecular interactions of the types C-H…O, O-H...O, N-H…O and N-H…N/C-H…F/C-H…Cl as observed in quinoline molecules (1-25) and presented in Table 5, it has been observed that the N and O atoms are the predominant hydrogen bond donor and acceptor, respectively. The overall d(H…A) range lies between 1.75 and 2.81Å, the D(X…A) range is between 2.625 and 3.451Å, and the angular range Θ(X-H…A) falls between 103 and 176.5°. The range of values for d, D and Θ as exist in case of C-H…O, O-H...O, N-H…O and N-H…N/C-H…F/C-H…Cl intra- and intermolecular interactions is presented in Table 5.

The atom C acts as the most predominant hydrogen donor with frequency of occurrence at 66.7% and the O atom acts as hydrogen acceptor with frequency of occurrence at 100%. The range for d(H…A), D(X…A) and angular range Θ(X-H…A) for C-H…O and O-H…O intermolecular hydrogen bonds is presented in Table 6. In the case of intermolecular interactions, it has also been observed that the N atom acts as the most predominant hydrogen donor with frequency of occurrence 76.19% and the O atom acts as hydrogen acceptor with frequency of occurrence 90.47%.The overall range d(H…A) lies between 1.75 and 2.57 Å, the D(X…A) range is between 2.625 and 3.511 Å and angular range Θ(X-H…A) falls between 103.0 and 174.0°. The range for d(H…A), D(X…A) and angular range Θ(X-H…A) for C-H…O, N-H…O and N-H…N intermolecular hydrogen bonds are presented in Table 6.

2.2. Graphical presentation of interactions

The key structural feature distinguishing the hydrogen bond from the other non-covalent interactions is its preference for linearity [40]. A better way to analyse preferences, is to draw d-Θ and D-Θ scatter plots. The plots include all contacts found in molecules (1-25) with d< 2.57Å and D<3.511Å at any occurring angle. The graphical projections of d-Θ [d(H…A) against Θ (X-H…A)] and D-Θ [D(X…A) against Θ (X-H…A)] scatter plots have been made for intermolecular interactions which are shown in Figure 3(a,b).

The following observations have been made:

(i) The density of spots for d(H…A) [=1.87-2.39Å] and D(X…A) [=2.835-3.511 Å] is presented in the theta [Θ(X-H…A)] range ~143.0-173.3^o in the case of N-H…O hydrogen bonds.

(ii) The density of spots for C-H…O intermolecular hydrogen bonds is quite high in a given range of values for d(H…A)= 2.39-2.57 Å, D(X…A)= 3.239-3.429 Å and Θ(X-H…A)= 133.0^o-152.0^o.

(iii) The relative frequency of occurrence of various types of N-H…O, C-H…O, O-H…O, N-H…N, O-H…N and C-H…Cl intermolecular hydrogen bond is 71.43, 16.67, 2.38, 4.76, 2.38 and 2.38%, respectively and it is shown in figure 4.

Table 1: CSD code, chemical name, chemical formula, molecular wt. and reference of molecules (1-25)

Molecule	Refrence Code	Chemical Name	Chemical Formula	Molecular Weight	Reference
M-1	BUFBOU	(RS)-3-Acetyl-2-methyl-4-(3-nitrophenyl)-1,4,5,6,7,-hexahydroquinolin-5-one	$C_{18}H_{18}N_2O_4$	326.34	13
M-2	CUBNIX	t-Butyl 2,6,6-trimethyl-4-(2-fluoro-3-chloro-5-(trifluoromethyl)phenyl)-5-oxo-1,4,5,6,7,8-hexahydro quinoline-3-carboxylate	$C_{24}H_{26}Cl_1F_4N_1O_3$	487.92	14
M-3	DAYJIX	(+-)-ethyl 4-(2,3-difluoro Phenyl)-2,6,6-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro quinoline-3-carboxylate	$C_{21}H_{23}F_2N_1O_3$	375.41	15
M-4	FERHEQ	Methyl 4-(3-bromo-4-fluorophenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydro quinoline-3-carboxylate	$C_{18}H_{17}Br_1F_1N_1O_3$	394.24	16
M-5	HAKXOI	Ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate	$C_{21}H_{24}Cl_1N_1O_3$	373.86	17
M-6	KITRIP	Methyl 1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(3,4,5-trimeth oxy phenyl)-5(6H)-oxoquinolin-3-carboxylate	$C_{23}H_{29}N_1O_6$	415.47	18
M-7	LAQTOO	DL-Methyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate	$C_{21}H_{25}N_1O_4$	355.42	19
M-8	LAVWIP	Methyl 2-methyl-5-oxo-4-p-tolyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate	$C_{19}H_{21}N_1O_3$	311.37	20
M-9	LOQCAX	ethyl 4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate	$C_{21}H_{24}Br_1N_1O_3$	418.32	21
M-10	LOQCEB	ethyl 4-(3-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate	$C_{21}H_{24}Br_1N_1O_3$	418.32	21
M-11	NEQYEP	2-Amino-7,7-dimethyl-5-oxo-4-(3-(trifluoromethyl)phenyl)-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile	$C_{19}H_{18}F_3N_3O_1$	361.36	22
M-12	PAHYIH	Methyl 4-(2-chloro-5-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-	$C_{20}H_{21}Cl_1N_2O_5$	404.85	23

		carboxylate			
M-13	PUGCIE	Ethyl 4-(3-hydroxyphenyl)-2, 7,7-trimethyl-5-oxo-1,4,5,6,7, 8-hexahydroquinoline-3- carboxylate	C_{21} H_{25} N_1 O_4	355.42	24
M-14	QANWEI	Methyl 2,7,7-trimethyl-5-oxo -4-(3-chlorophenyl)-1,4,5,6,7, 8-hexahydroquinoline-3- carboxylate	C_{20} H_{22} Cl_1 N_1 O_3	359.84	25
M-15	SUYWIT	Ethyl 2-methyl-5-oxo-4-(3,4,5 -trimethoxyphenyl)-1,4,5,6,7, 8-hexahydroquinoline-3- Carboxylate	C_{22} H_{27} N_1 O_6	401.44	26
M-16	TEJQII	Methyl 2,7,7-trimethyl-4-(3-nitro phenyl)-5-oxo-1,4,5,6,7,8-hexa hydroquinoline-3-carboxylate	C_{20} H_{22} N_2 O_5	370.40	27
M-17	TEJQOO	3-Acetyl-2,7,7-trimethyl-4- phenyl-1,4,5,6,7,8-hexahydro- 5-quinolone	C_{20} H_{23} N_1 O_2	309.41	27
M-18	TOWKAT	ethyl 4-(4-hydroxyphenyl)-2, 7,7-trimethyl-5-oxo-1,4,5,6, 7,8-hexahydroquinoline-3- carboxylate	C_{21} H_{25} N_1 O_4	355.42	28
M-19	UCOLOO	(RR,SS)-methyl 4-(2,4-chloro phenyl)-2,7-dimethyl-5-oxo-1,4, 5,6,7,8-hexahydroquinoline-3- carboxylate (RS,SR)-methyl 4- (2,4-chlorophenyl)-2,7-dimethyl -5-oxo-1,4,5,6,7,8-hexahydro quinoline-3-carboxylate	C_{19} H_{19} Cl_2 N_1 O_3	380.27	29
M-20	UJAHIY	2-Amino-7,7-dimethyl-4-(4-nitro phenyl)-5-oxo-1,4,5,6,7,8-hexa hydroquinoline-3-carbonitrile N, N-dimethyl formamide solvate	C_{18} H_{18} N_4 O_3, C_3 H_7 N_1 O_1	411.46	30
M-21	VUZRIS	Methyl 4-(4-methoxyphenyl)-2- methyl-5-oxo-1,4,5,6,7,8-hexa hydro quinoline-3-carboxylate	C_{19} H_{21} N_1 O_4	327.37	31
M-22	WIGWIU	Ethyl 4-(5-bromo-2-hydroxy phenyl)-2,7,7-trimethyl-5-oxo -1,4,5,6,7,8-hexahydro quinoline-3-carboxylate	C_{21} H_{24} Br_1 N_1 O_4	434.32	32
M-23	XAYVEA	Ethyl 2,7,7-trimethyl-5-oxo- 4-phenyl -1,4,5,6,7,8-hexa hydroquinoline-3-carboxylate	$C_{21}H_{25}NO_3$	339.42	33
M-24	YASDAY	2-Amino-7,7-dimethyl-5-oxo -4-phenyl-1,4,5,6,7,8-hexa hydroquinoline-3-carbonitrile hemihydrates	C_{18} H_{19} N_3 O_1, 0.5(H_2 O_1)	302.37	34
M-25	YIYDUH	t-butyl 4-(4-methoxyphenyl)-2- methyl -5-oxo-1,4,5,6,7,8-hexa hydroquinoline-3-carboxylate	C_{22} H_{27} N_1 O_4	369.45	35

"Table 2. N1-C2, C2-C3, C3-C4, C4-C4a, C4a-C5, C5-C6, C6-C7 and C7-C8 bond distances (Å) for molecules (1-25)"

Bond distances (Å)								
N1-C2	C2-C3	C3-C4	C4-C4a	C4a-C5	C5-C6	C6-C7	C7-C8	
	sp^3-sp^2	sp^2-sp^2	sp^2-sp^3	sp^3-sp^2	sp^2-sp^3	sp^3-sp^3	sp^3-sp^3	sp^3-sp^3
M-1	1.391	1.350	1.51	1.50	1.41	1.54	1.57	1.56
M-2	1.387	1.352	1.52	1.51	1.43	1.52	1.53	1.51
M-3	1.381	1.359	1.52	1.52	1.45	1.53	1.53	1.51
M-4	1.408	1.358	1.51	1.53	1.45	1.54	1.44	1.46
M-5	1.385	1.347	1.52	1.51	1.43	1.50	1.52	1.53
M-6	1.389	1.350	1.52	1.51	1.44	1.51	1.52	1.52
M-7	1.390	1.346	1.52	1.51	1.43	1.52	1.53	1.52
M-8	1.388	1.357	1.52	1.52	1.45	1.51	1.52	1.52
M-9	1.391	1.351	1.53	1.52	1.44	1.52	1.53	1.53
M-10	1.386	1.357	1.52	1.52	1.45	1.51	1.54	1.53
M-11	1.378	1.362	1.52	1.50	1.45	1.50	1.53	1.53
M-12	1.387	1.355	1.52	1.52	1.45	1.51	1.53	1.54
M-13	1.380	1.354	1.53	1.51	1.44	1.50	1.53	1.52
M-14	1.391	1.352	1.52	1.51	1.44	1.51	1.53	1.53
M-15	1.379	1.356	1.53	1.51	1.45	1.51	1.51	1.51
M-16	1.390	1.356	1.52	1.52	1.44	1.51	1.53	1.53
M-17	1.379	1.368	1.53	1.50	1.45	1.50	1.55	1.53
M-18	1.379	1.350	1.53	1.51	1.45	1.50	1.53	1.53
M-19	1.377	1.359	1.53	1.52	1.44	1.50	1.54	1.50
M-20	1.380	1.361	1.52	1.52	1.44	1.50	1.54	1.53
M-21	1.383	1.334	1.53	1.50	1.42	1.50	1.51	1.50
M-22	1.380	1.352	1.52	1.51	1.44	1.50	1.53	1.52
M-23	1.385	1.350	1.52	1.51	1.44	1.50	1.53	1.52
M-24	1.380	1.363	1.52	1.52	1.44	1.51	1.52	1.53
M-25	1.400	1.349	1.52	1.50	1.44	1.51	1.52	1.51

"Table 3. N1-C2-C3, C2-C3-C4, C3-C4-C4a, C4-C4a-C8a, C4a-C5-C6, C5-C6-C7, C6-C7-C8 and C7-C8-C8a bond angles (°) for molecules (1-25)"

Bond Angles (°)								
C2	C3	C4	C4a	C5	C6	C7	C8	
Mol. sp^2	sp^2	sp^3	sp^2	sp^3	sp^3	sp^3	sp^3	
M-1	118.9	120.8	111.3	122.5	118.2	106.6	116.2	105.4
M-2	120.1	121.7	111.4	120.5	120.4	109.1	112.5	111.1
M-3	119.5	120.6	110.8	120.5	119.9	111.4	113.4	111.2
M-4	116.5	122.3	110.8	120.4	117.4	113.6	116.8	111.8
M-5	119.8	121.0	110.5	119.2	119.1	115.3	107.9	113.1
M-6	119.4	119.2	109.8	119.5	117.9	114.8	107.9	112.4
M-7	119.6	122.1	109.7	119.8	118.0	114.5	108.3	113.3
M-8	119.2	120.5	109.4	119.7	118.5	112.6	109.6	110.5
M-9	120.5	121.0	110.5	119.9	118.7	115.3	108.3	113.2
M-10	119.7	120.5	109.0	119.6	118.6	115.3	108.4	112.8
M-11	119.1	122.5	109.2	119.8	118.1	113.6	107.4	112.9
M-12	119.9	121.3	109.8	120.2	117.6	113.2	108.2	113.2
M-13	119.2	121.7	110.4	119.4	118.5	114.6	107.4	113.5
M-14	119.3	121.3	110.0	120.0	118.0	114.2	107.6	113.2
M-15	119.6	120.8	110.4	119.7	118.3	113.8	110.8	111.4
M-16	119.4	121.2	110.2	120.4	117.3	114.4	108.2	113.8
M-17	120.2	119.3	110.6	119.4	117.2	114.6	106.5	113.1
M-18	119.2	121.8	109.8	119.4	118.0	114.5	107.3	113.3
M-19	120.1	122.1	110.8	119.0	119.0	114.6	108.3	113.0

M-20	120.1	121.8	109.1	119.3	119.0	113.9	107.8	113.7
M-21	120.4	121.3	112.2	120.0	119.1	114.0	110.6	111.4
M-22	119.2	120.9	110.6	119.5	118.6	113.5	107.7	113.1
M-23	119.5	120.6	109.6	124.1	118.5	115.3	107.8	113.4
M-24	119.3	122.7	109.3	118.8	118.7	114.8	107.9	113.2
M-25	119.6	119.7	109.4	120.1	117.8	111.9	110.6	110.5

"Table 4. Different types of conformations in the individual rings of Quinoline moiety (molecules 1-25)"

Molecule	Ring A (conformation)	Ring B (conformation)
M-1	Sofa	Half-chair
M-2	Boat	Sofa
M-3	Shallow boat	Envelope
M-4	Sofa	Half-chair
M-5	Sofa	Sofa
M-6	Half-chair	Half-chair
M-7	Flat boat	Sofa
M-8	Boat	Envelope
M-9	Flat boat	Envelope
M-10	Flat boat	Envelope
M-11	Sofa	Sofa
M-12	Shallow boat	Intermediate between envelope and half-chair
M-13	Boat	Envelope
M-14	Boat	Half-chair
M-15	Boat	Envelope
M-16	Boat	Intermediate between sofa and Half-chair
M-17	Boat	Intermediate between sofa and Half-chair
M-18	Half-chair	Half-chair
M-19	Boat	Envelope
M-20	Sofa	Sofa
M-21	Screw boat	Envelope
M-22	Half boat	Half boat
M-23	Sofa	Sofa
M-24	Distorted boat	Envelope
M-25	Pseudo boat	Sofa

"Table 5. Geometry of C-H…O, O-H...O, N-H…O and N-H…N/C-H…F/C-H…Cl intra- and intermolecular interactions"

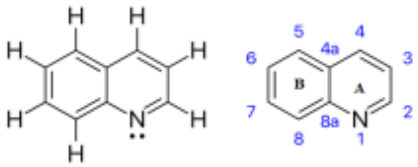
Molecule [Number of Donors and Acceptors]	Intramolecular interaction (X-H…A)	H…A(Å) d	X…A(Å) D	X-H…A(°) Θ
M-20 UJAHIY Donors=3 Acceptors=1	C8-H8B…O4	2.56	3.331	103
	C24-H24B…O4	2.38	2.756	136
	C14-H14…O4	2.475	3.349	157
M-21 VUJRIS Donor=1 Acceptor=1	C10-H10A…O3	2.08	2.818	132
M-22 WIGWIU Donor=1 Acceptor=1	O4-H4…O1	1.75	2.625	171
M-24 YASDAY Donor=1 Acceptor=1	O3-H3C…O1	2.02	2.763	146

	Intermolecular interactions			
M-1	N1-H2A…O3	2.06	2.927	173
BUFBOU	C6-H6…O4	2.56	3.309	138
Donors=4	C18-H18A…O1	2.46	3.239	138
Acceptors=3	C18-H18B…O3	2.57	3.422	148
	C7-H11A…O1	2.55	3.290	133
M-2	N1-H31…O5	2.060	2.904	173.3
CUBNIX				
Donor=1				
Acceptor=1				
M-3	N1-H1…O5	2.04	2.945	168
DAYJIX				
Donor=1				
Acceptor=1				
M-4	N1-H1…O1	2.057	2.947	155.31
FERHEQ				
Donor=1				
Acceptor=1				
M-5	N1-H1…O3	1.976	2.835	176.5
HAKX01				
Donor=1				
Acceptor=1				
M-6	N1-H1…O6	2.057	2.917	161.9
KITRIP				
Donor=1				
Acceptor=1				
M-7	N1-H0A…O1	2.019	2.868	168.7
LAQTOO				
Donor=1				
Acceptor=1				
M-8	N1-H1…O1	2.02	2.834	160
LAVWIP				
Donor=1				
Acceptor=1				
M-9	N1-H1…O1	1.94	2.812	168
LOQCAX				
Donor=1				
Acceptor=1				
M-10	N1-H1…O1	2.05	2.889	166
LOQCEB				
Donor=1				
Acceptor=1				
M-11	N1-H1…O1	2.39	3.117	143
NEQYEP	N16-H16A…N20	2.12	2.966	168
Donors=2	N16-H16B…O1	2.08	2.897	158
Acceptors=2				
M-12	N1-H1…O5	2.12	2.908	156
PAHYIH				
Donor=1				
Acceptor=1				
M-13	O8C-H8C…O9B	2.05	2.835	162
PUGCIE	N1-H1…O6A	2.16	2.970	157
Donors=2				
Acceptors=2				
M-14	N1-H1…O1	2.07	2.884	154
QANWEI	C20-H20A…CL1	2.81	3.511	129
Donors=3	C13-H13…O2	2.39	3.260	152
Acceptors=3				

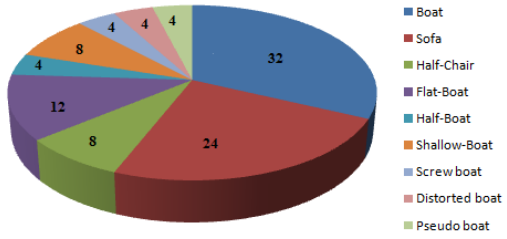
M-14 QANWEI Donors=3 Acceptors=3	N1-H1…O1 C20-H20A…CL1 C13-H13…O2	2.07 2.81 2.39	2.884 3.511 3.260	154 129 152
M-15 SUYWIT Donors=3 Acceptors=2	N1-H1N…O1 C8-H2B…O4 C10-H10B…O1	2.21 2.55 2.59	2.995 3.340 3.429	160 138 146
M-16 TEJQII Donor=1 Acceptor=1	N1-H1…O1	2.21	3.054	165
M-17 TEJQOO Donor=1 Acceptor=1	N1-H1…O1	2.21	3.054	165
M-18 TAWQAT Donor=1 Acceptor=1	N1-H1A…O1	2.041	2.888	168.01
M-19 UCOLOO Donor=1 Acceptor=1	N1-H1…O5	1.96	2.835	173
M-20 UJAHIY Donors=2 Acceptor=1	N19-H19A…O1 N1-H1…O1	2.02 2.13	2.840 2.911	156 150.2
M-21 VUJRIS Donor=1 Acceptor=1	N1-H0A…O1	2.05	2.884	163
M-22 WIGWIU Donor=1 Acceptor=1	N1-H1…O2	2.05	2.866	158
M-23 XAYVEA Donor=1 Acceptor=1	N1-H1…O1	2.04	2.890	168
M-24 YASDAY Donors=5 Acceptors=5	N6-H6B…O1 N1-H1…O2 N3-H3A…N2 N3-H3B…O2 O3-H3D…N5 N4-H4…O3	2.09 2.14 2.15 2.14 2.16 1.87	2.911 2.892 2.990 2.927 2.935 2.744	156 144 159 148 152 174
M-25 YIYDUH Donor=1 Acceptor=1	N1-H12…O4	2.00	2.884	164

"Table 6. Range for d(H…A), D(X…A) and Θ(X-H…A) for C-H…O, O-H…O, N-H…O and N-H..N intra- and intermolecular hydrogen bonds"

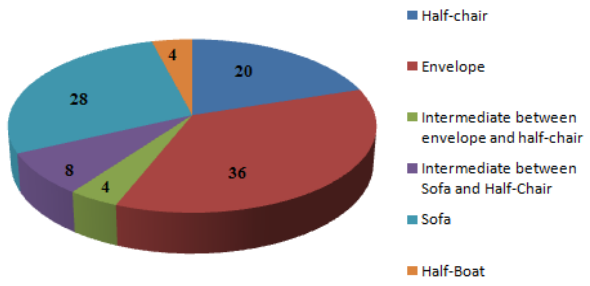
Type of bond	d(H...A) range(Å)	D(X...A) range (Å)	Θ(X-H...A) range(°)
Intramolecular			
C-H…O	2.08-2.56	2.756-3.349	103.0-157.0
O-H…O	1.75-2.02	2.625-2.763	146.0-171.0
Intermolecular			
C-H…O	2.39-2.57	3.239-3.429	133.0-152.0
N-H…N	2.12-2.15	2.990-2.966	159.0-168.0
N-H…O	1.87-2.39	2.835-3.511	143.0-174.0



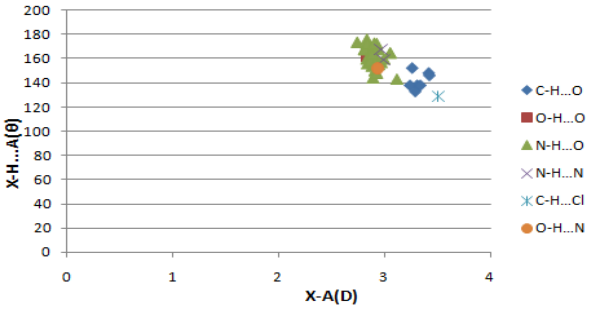
"Figure-1: Basic quinoline molecule (C9) with atomic numbering scheme"



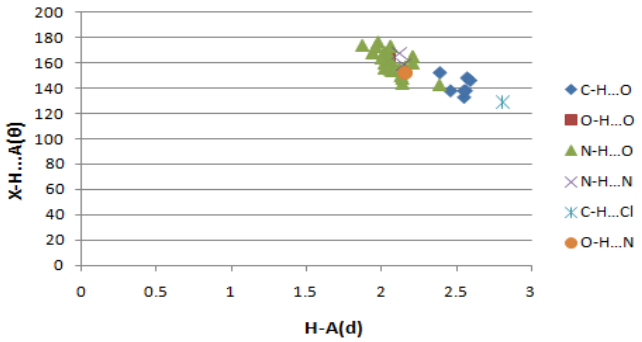
"Figure 2(a). Relative frequency of occurrence (in %) for various types of conformations in six-membered ring A (molecules 1-25)"



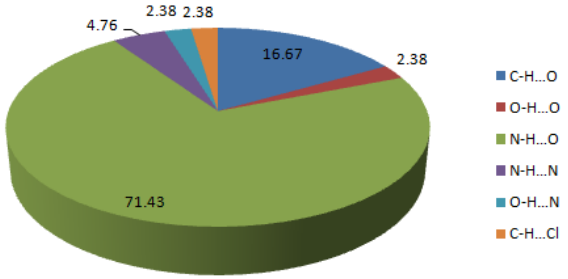
"Figure 2(b). Relative frequency of occurrence (in %) for various types of conformations in six-membered ring B (molecules 1-25)"



"Figure 3(a). d-Ɵ scatter plot for intermolecular C-H…O, O-H…O, N-H…O, N-H…N, C-H…Cl and O-H..N hydrogen bonds"



"Figure 3(b). D-Ɵ scatter plot for intermolecular C-H…O, O-H…O, N-H…O, N-H…N, C-H…Cl and O-H..N hydrogen bonds"



"Figure 4. Relative frequency of occurrence (in %) for various types of intermolecular hydrogen bonds"

3. CONCLUSION

On comparison of some geometrical features of the series of quinoline derivatives, it is found that substituents are located mostly at C2 & C7 position of the quinoline nucleus. Hydrogen bonding interactions are present in these molecules and the substituents (at the C2 & C7 position) which are involved in these interactions may be responsible for the lengthening and shortening of bond distances N1-C2, C2-C3, C6-C7 and C7-C8. Hydrogen bonding may also be responsible for deviation of N1-C2-C3 and C6-C7-C8 bond angles from its normal value. The bending in this bond angle typically amounts to only few degrees, which resembles the results shown by Desiraju and Steiner [41]. Stress has been laid to study the hybridization (single/double bond) and ring fusions for the conformation of individual ring systems and stability of quinoline molecules.

On comparing the hydrogen bond interactions, it is also concluded that the N-H…O hydrogen bonding is quite predominant in quinoline class of alkaloids and the frequent contacts from H(N) atoms have a statistical preference to 'O' as donor. The design of new molecules with desired properties is the future intention of chemists/ crystallographers which requires the understanding of intermolecular interactions in crystal packing. Thus, understanding of intermolecular interactions becomes important.

4. ACKNOWLEDGEMENTS

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