

Chapter 11

Structure Property Relationship

This chapter summarizes the important results from the structural studies of nitrenium compounds and a mesogen. The compounds which we have been studied are listed in Figure 12.1.

The bond angles and bond distances of five membered ring is compared with the reported structures of 1,3-dimethylbenzotriazolium iodide(3) and 1-benzyl-3-methyltriazolium-iodide(4)[68]. There are observable variations in bond angles and distances with respect to the above two structures of the five membered ring compounds. The angle N1 — N2 — N3 is widened in case of 3 as compared with 4. The rest of the angles show no deviation. And also bond distances N1 — N2 and N2 — N3 are smaller in 3 as compared with that of 4.

When we compare the structure of 5 with 3 and 4. the bond angle N1 — N2 — N3 of 5 is smaller than that in 3 and it is equal to that of 4. A similar, however stronger narrowing as at N2 is observed at the carbene C2 atoms of the Arduengo carbenes 1a. The bond distance of N1 — N2 and N2 - N3 in 3 are 1.323(1)Å and 1.326(1) Å respectively and are same as in 3 and 4. This shows strong delocalization within N1 — N2 — N3 framework of this species. The comparison of structures of 6 and 7 with 3 and 4 we notice that the bond angle N1 - N2 - N3 in 6 is 109.0(3)° and it is larger than that

Table 11.1: Comparison of Bond lengths and angles

| | 1 | 2 | 3 | 4 | 5 |
|----------|----------|----------|----------|----------|----------|
| N1-N2 | 1.302(6) | 1.316(3) | 1.323(1) | 1.278(4) | 1.320(1) |
| N2-N3 | 1.320(5) | 1.319(3) | 1.326(1) | 1.300(4) | 1.307(7) |
| N3-C4 | 1.368(5) | 1.343(4) | 1.350(1) | 1.416(5) | 1.366(8) |
| C4-C5 | 1.385(6) | 1.355(4) | 1.348(1) | 1.519(2) | 1.383(8) |
| C5-N1 | 1.364(6) | 1.342(3) | 1.334(1) | 1.461(5) | 1.343(7) |
| N1-N2-N3 | 106.3(3) | 103.8(2) | 103.8(7) | 109.0(3) | 105.5(6) |
| N2-N3-C4 | 111.4(3) | 112.4(2) | 113.5(9) | 113.7(3) | 111.5(6) |
| N3-C4-C5 | 105.0(4) | 105.7(2) | 104.0(1) | 101.4(3) | 105.5(6) |
| C4-C5-N1 | 105.2(4) | 105.4(2) | 104.0(1) | 101.5(4) | 104.5(6) |
| C5-N1-N2 | 112.1(4) | 112.7(2) | 115.1(1) | 114.4(4) | 112.8(5) |

in **3** and **4**. Bond lengths are N1 - N2 and N2 - N3 in **6** are 1.278(4)Å and 1.300(4) Å respectively and are smaller than those to **3** and **4**. Bond lengths N1 - N2 and N2 - N3 for **7** are 1.323(1) Å and 1.326(1) Å respectively and are widened when compared with **3** and **4**.

It is interesting to study the effect of substituents on 1,2,3-triazole moiety. The bond angle N1 — N2 — N3 is widened for all substituents (**8**, **9**, **10**) when compared with 1,2,3-triazole. The bond distances N1 — N2 and N2 - N3 are shorter in **8**, **9**, **10** than in 1,2,3-triazole(**11**), while the N3 — C4 and N1-C5 are of comparable magnitude. The distance of C4-C5 bond is narrower than that in 1,2,3-triazole.

The crystal structures of **5**, **6**, **7** show that the anion is not directly connected to the positively charged part of the respective cation. In all the cases anion holds the respective cations by means of C — H.....I, C — H.....ClO₄⁻, C — H.....CF₃SO₃⁻, hydrogen bonds[73, 74]. This shows hydrogen bonding is prominent in nitrenium ions. The crystal structures of **5**, **6**, **7** compounds indicate that they are very stable. The results also fit into the picture of the structurally related carbenes **1a** which emerge from experimental and theoretical data. Thus stable nitrenium ions (as their

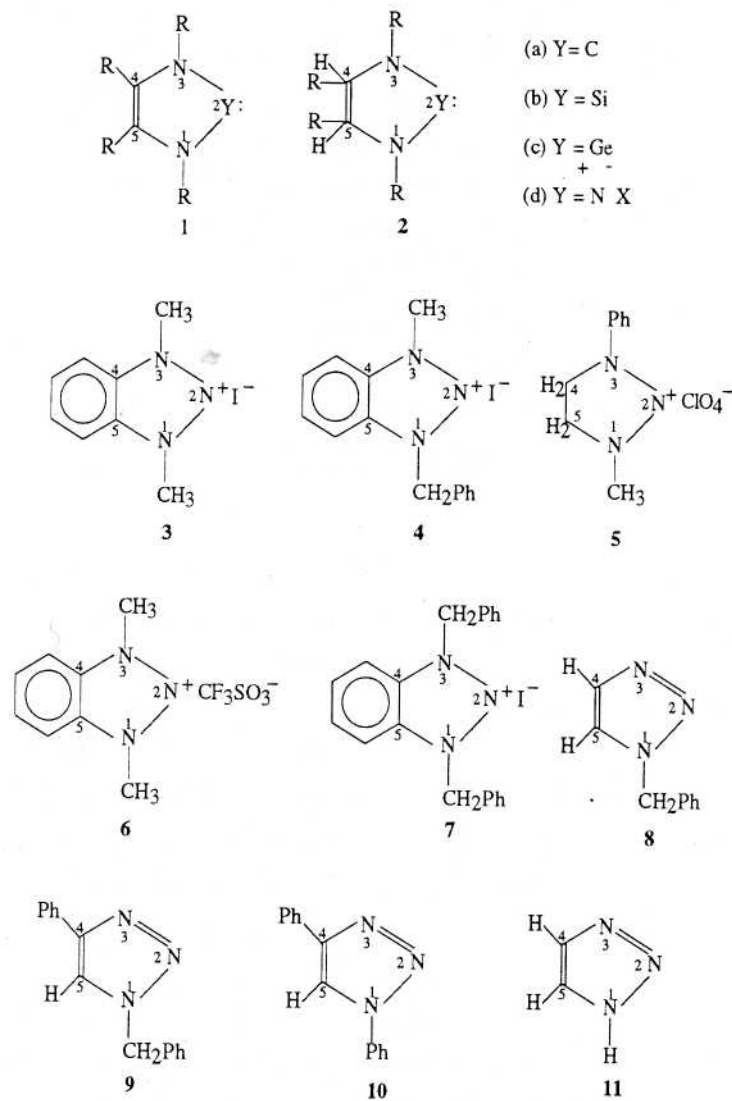


Figure 11.1:

Table 11.2: Comparison of Bond lengths and angles

| | 6 | 7 | 8 | 9 |
|-----------|-------|----------|----------|----------|
| N1-N2 | 1.352 | 1.323(6) | 1.371(4) | 1.314(3) |
| N2-N3 | 1.331 | 1.347(4) | 1.342(4) | 1.359(8) |
| N3-C4 | 1.362 | 1.335(5) | 1.292(4) | 1.361(8) |
| C4-C5 | 1.383 | 1.350(6) | 1.330(4) | 1.358(8) |
| C5-N1 | 1.356 | 1.360(6) | 1.393(4) | 1.363(8) |
| N1-N2-N3 | 106.3 | 107.3(3) | 110.6(3) | 107.8(7) |
| N2-N3-C4 | 108.8 | 110.2(3) | 107.6(3) | 109.5(5) |
| N3-C4-C5 | 109.4 | 105.9(3) | 110.3(3) | 105.2(2) |
| C4-C5-N1- | 103.3 | 108.6(4) | 108.6(3) | 109,0(5) |
| C5-N1-N2 | 112.3 | 108.0(3) | 112.9(3) | 108.5(7) |

carbene analogues) are electronically distinct from normal ones.

One of the most intriguing questions with respect to carbenes of the type **1a** and **2a** concerns their electronic structure. Besides several conflicting reports on (theoretical) investigations and their interpretation, dealing with the amount of (cyclic) delocalization in these species, two recent publications come to conclusion that the saturated Wanzlick carbenes of the type **2a** are well stabilized through π -donation by the two amino substituents and that carbenes **1a** of the Arduengo type profit additionally from cyclic delocalization (partial aromaticity).

The structure of Di-(2,7-substituted -9-flourenyl) glutamate shows a strong imbrication of the molecules as expected for a nematogenic mesogen. This kind of packing in solid state may explain the reentrant nematic phase exhibited by the substance through sequential disruption of the types of imbrication. The crystalline cohesion is due to both dipole-dipole and dispersion interaction.

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$$\sqrt{\Sigma w(|F_o| - |F_c|)^2 / (N_o - N_v)}$$

where, N_o = number of observations N_v = number of variables

- [129] Function minimized: $\sum w(|F_o| - |F_c|)^2$

$$w = \frac{1}{\sigma^2(F_o)} = [\sigma_c^2(F_o) + \frac{p^2}{4} F_o^2]^{-1}$$

$\sigma_c(F_o)$ = e.s.d. based on counting statistics p = p-factor

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