Chapter V

Number of $\pi$-bonds in a Molecules: Their extent of Delocalization: Symmetric screening leading to Localization of $\pi$-electron density
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NUMBER OF \( \pi \) BONDS IN A MOLECULE: THEIR EXTENT OF
DELOCALIZATION: SYMMETRIC STRETCHING LEADING TO LOCALIZATION
OF \( \pi \) ELECTRON DENSITY

It has been noted that molecules having double bonds
(characterized by one \( \sigma \) bond and one \( \pi \) bond) have a
prominent property of odor. It is noted that if there are
two bonds lying side by side they produce a much heavier
odor intensity then two double bonds away from each other:
e.g., Alkyl - \( 2^t - 4^t \) dienal \( 0.09 \) \( \mu \) values

Alkyl - \( 2^t - 6^c \) dienal \( 0.01 \)

The presence of \( \sigma \) bonds in molecules have much lower
odor sometimes or have no odor but molecule containing
bonds have distinct odor as is known of the compounds:

\[ \text{C}_2\text{H}_6, \text{C}_2\text{H}_4, \text{C}_2\text{H}_2 \]

The place of a double bond within a molecule will
have its effect on the type of odor and as such, this will
lead to make some difference in some distribution of \( \pi \)
electron density at different points in the molecule. This
is well illustrated by the following examples:
Eugenol, isoeugenol and $\alpha$ and $\beta$ ionone which are distinct as reported by Moncrieff\textsuperscript{3}. It has been noted that reduction of an unsaturated bond of a body reduces the odor. e.g. odor of dihydrocoumarin < coumarin\textsuperscript{4}.

One doubt is created by Moncrieff himself\textsuperscript{5}. Is chemical unsaturation necessary for odor? The answer is it may or may not be necessary but, of course, for prominent odors (pungent) unsaturation is a must. It is also said that ether has powerful odor. Yet it's constitution shows no trace of unsaturation. At this stage, the problem is not to search for unsaturation but to look at the possibility of electrons of the $p$ character taking part in the molecule.

In the molecule of $C_2H_6$ (ethane) there is no $\pi$ bond present but $sp^3$ orbital of one carbon when uniting with $sp^3$ orbital of another carbon would have definitely some $p$-character and it may be predicated that if a substance has slightest odor there should be some degree of $p$ electrons which would be in delocalized form. The proof can be obtained in an indirect way. If we assume that delocalization is removed with interaction of metallic element like sodium (Na) it would bring in deodorization, by localizing the charge cloud.

For example, acetophenone has characteristic odor while sodium salt is solid and odorless (Tested by us). Similarly, silver acetylide has also no odor, because electron of silver (Ag) interacts with the $p$ electrons of acetylene and the same
will be true for copper and platinum acetylenes where d electron orbitals of copper and also Pt metals appear to interact with p electrons of \( C_2H_2 \).

An argument similar to \( C_2H_2 \) should be applicable to explain the powerful smell available in the ethers despite of no trace of unsaturation.

The symmetric stretching appears to lower the odor intensity is clear from the illustration that m-tolylthiocarbimide is pungent but its isomer p-tolylthiocarbimide has a sweet anise odor. This can be explained on the ground that the \( -CH_3 \) group has a symmetric stretching over the delocalized clouds and therefore, part of the delocalization will get localized and hence the molecule p-tolylthiocarbimide has sweet anise odor.

The combined effect of number of p bonds and symmetric stretching can well be illustrated by considering the odor of \( C_6H_6 \), 1:3 dihydrobenzene, 1:4 dihydrobenzene, tetrahydrobenzene and cyclohexane. The following odor is found for odor-intensity.

\[
\text{dihydrobenzene} > \text{dihydro benzene} > \text{benzene} > \text{tetrahydro benzene} > \text{cyclohexane}
\]
The powerful odor of benzene compared with the paraffin hexane is due to its ring structure as well as to the unsaturation, for benzene can be hydrogenated by a roundabout method to 1,3 dihydrobenzene, which has only two double bonds compared with three in benzene, and yet its odor is distinctly stronger and pungent than that of benzene itself.

An isomeric 1,4 dihydrobenzene is also known, and this has a less pungent odor than its 1,3 isomer, and is more comparable in odor with the tetrahydrobenzene. Further hydrogenation reduces the odor intensity compared with 1,3 dihydrobenzene, but it is still pungent, whilst complete reduction to cyclohexane reduces the odor again so that it is now comparable with that of the original benzene in intensity, but blander and more fatty in character.

It can be noted that 1,3 dihydrobenzene has two double bonds but not symmetrically localized as compared to isomer which has two double bond symmetrically located, has a odor less than 1,3 dihydrobenzene. The odor of 1,4 dihydrobenzene is greater than C6H6. The lowering in odor intensity of C6H6 is due to three double bonds in a system of six carbons which tries to give a greater symmetry as compared to 1,4 dihydrobenzene and, therefore, even when the number of double bonds (clouds) is more, the clouds appear to be more localized as compared to 1,4 dihydrobenzene which is reflected in odor property. It is very much possible
that we can consider the odor property as a guidance in deciding other structural properties.

Thus number of $p \pi$ clouds (no of $p \pi$ bonds) and their delocalization decided by the symmetric stretching will answer some problems of odor intensity for molecules with some structural features in common.

The symmetric stretching of $\pi$ clouds reduces odor as can be clearly seen from the illustration of trans-butene and cis-butene. The trans-butene has a threshold value of $3.5 \times 10^{-4}$ while cis-butene-2- has a threshold value of $4.0 \times 10^{-6}$. About 100 fold difference in threshold value of cis and trans-butene-2- can be explained on the basis that there is symmetric stretching of the delocalized $\pi$-clouds and, therefore, lower odor. This is also well illustrated by considering the symmetric stretching in a sym-ketone as compared to the muscone which has a nice fragrant smell. The symmetric ketone has no smell as reported by Roderick.

\[
\begin{align*}
  &\text{muscone} & &\text{symmetric ketone} \\
  \begin{array}{c}
    \text{H}_3\text{C} \cdot \text{CH} \\
    \text{(CH}_3)_2
  \end{array} & & & &
  \begin{array}{c}
    \text{CH}_2 \\
    \text{C} = \text{O}
  \end{array} & & & &
  \begin{array}{c}
    \text{CH}_2\text{C} \cdot \text{O} \\
    \text{(CH}_3)_2
  \end{array} & & & &
  \begin{array}{c}
    \text{CH}_2 \\
    \text{C} = \text{O}
  \end{array}
\end{align*}
\]
The odor intensity in napthalene and its hydrogenated products indicated that less the number of \( p \)-clouds lower the odor intensity.

\[
C_{10H_8} \rightarrow C_{10H_{12}} \rightarrow C_{10H_{13}}
\]

napthalene tetra-deca hydronaphthalene hydronaphthalene (declain) (tetralin)

The most illustrious example of symmetric charge cloud stretching in reducing odor property is the no-odor of carnone.

The unsymmetric stretching or the imbalance high odor strength and lower threshold values. This is best illustrated by the pyrazine derivatives whose odor threshold values have been given by Teranishi.
Structure and threshold values of pyrazine compounds.

- Pyrazine: 175,000,000
- 2,5 dimethyl pyrazine: 1,300,000
- 2-isobutylpyrazine: 4,000,000
- 2-isobutyl-3-methyl pyrazine: 35,000
- 2-methoxy-3-isobutyl pyrazine: 2

Of course, Teranishi and coworkers simply considered that increase in the number of carbon atoms in the chain reduced the threshold value. But actually, adding more carbon atoms would only increase the size of the molecule and cannot
give rise to about 3 stages of 100 fold variation in the series of molecules related to 2-methoxy-3-alkylpyrazines originating from pyrazine itself. Hence, some effect of symmetric stretching on the $p$-electron charge clouds will have to be considered. The same is well illustrated for a series of thiazoles. Similar to pyrazine series in the thiazoles the unsubstituted ring has the highest threshold and as the number of groups in the ring increases, the threshold decreases. This can be clearly looked upon from the geometric point of view. In fact, small structural changes in the thiazole derivatives which may be present in different foods such as filberts, peanuts and coffee are due to these changes. Thus, the odor character variations are also related with structural, geometrical and $\pi$ cloud stretching characteristics.

We had a chance to discuss the aspect of odor intensity problem at the 62nd Indian Science Congress when we invited some series of compounds from chemist members to predict the odor intensity. Prof. Devprabhakar of I.I.S. Bangalore gave us the following series of and our prediction was agreed upon by him.
1:5 cyclooctadiene  1:3 cyclooctadiene

The dipole moment is considered by Price\textsuperscript{15} as a measure of electrical dissymmetry in a molecule. The following are properties of cis-1,2-dichloroethylene and trans 1,2-dichloroethylene:

\[
\begin{align*}
\text{cis} & : \quad \begin{array}{c}
\text{Cl} \\
\text{H}
\end{array} \quad \begin{array}{c}
\text{C} \\
\text{H}
\end{array} \quad \begin{array}{c}
\text{Cl} \\
\text{H}
\end{array} \\
\text{trans} & : \quad \begin{array}{c}
\text{Cl} \\
\text{H}
\end{array} \quad \begin{array}{c}
\text{C} \\
\text{H}
\end{array} \quad \begin{array}{c}
\text{C} \\
\text{Cl}
\end{array}
\end{align*}
\]

Cis - 1,2 - dichloroethylene \hspace{1cm} trans- 1,2-dichloroethylene

<table>
<thead>
<tr>
<th>Property</th>
<th>cis</th>
<th>trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p.</td>
<td>-80°C</td>
<td>-50°C</td>
</tr>
<tr>
<td>(u) in debye</td>
<td>1.89</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Since Cl has stronger electron affinity than carbon for electron, the electron pair joining C-Cl will spend more time near Cl thus giving Cl a net negative charge and carbon a small positive charge. In the trans-isomer, the bond dipole moment thus created are equal and opposed to each other leading to no net dipole moment. In fact, the molecule is more covalent (non polar) but there is symmetric stretching of charge clouds and, therefore, delocalized charge clouds also gets partially localized and hence there will be decrease in odor as compared to cis isomer. On this basis, the cis isomer will have greater odor.
intensity as compared to the trans isomer. This can also be compared with cis and trans butenes where cis isomer has threshold value of $4.0 \times 10^{-6}$ while trans isomer has $3.5 \times 10^{-4}$ threshold value.

\[ \text{cis butene} \quad \text{trans butene} \]

\[
\begin{align*}
\text{cis butene:} & \quad \text{m.p.} \quad -139^\circ C \quad \text{b.p.} \quad 3.7^\circ C \\
\text{trans butene:} & \quad \text{m.p.} \quad -106^\circ C \quad \text{b.p.} \quad 0.9^\circ C
\end{align*}
\]

In butane trans and skew types of conformations are well known.

\[
\begin{align*}
\text{Skew}_1 & \quad \text{trans} \quad \text{Skew}_2
\end{align*}
\]

The energy diagram for conformations in butane has been given by Price\textsuperscript{16} as follows:
The energy difference between trans and skew forms for butane is 0.9 k cals/mole, while the barrier between skew form 1 is 3-5 k cals/mole and barrier between skew 2 form which places two \(-\text{Cl}_3\) groups in eclipsed conformation is between 4-5 to 6-1 k cals/mole.

Thus the energy differences are indicative of the degree of stability of the molecules in their specific conformation which ultimately depends upon the symmetric
stretching in the case of trans form which leads to a stabler molecule with lower energy. If this concept is extended the low odor of trans isomer can be clearly explained. The trans form is considered to be much stable and is found in the larger quantity than the skew forms.

In the case of 1,2-difluoro, 1,2-dibromo-, and 1,2-dichloroethane it has been experimentally estimated. The trans form is 53% while skew forms (skew, and skew2) to the extent of 48%.

The differences in odor for the axial and equatorial conformations of substances can also be explained on the basis of because the energy differences between the two forms, the equatorial form being more stable and it should have therefore, lower odor. Ohloff and Giersch have discussed that only diastereomers of dihydromabrinol series possess characteristic odor qualities. In all examples, 1,2,4-triaxial arrangement of the substituents in the decalin ring system (as shown below) is required, where one of these axial groups being an oxygen function.

![Diagram of decalin ring system with oxygen function](image-url)
The interchange of the methyl group and the angular hydrogen (Fig) reduces the odor qualities of sandalwood note\textsuperscript{18}.

Both trans-decalin derivatives (Fig. and ) in which the oxygen function occupies the angular position have typical mostly wet earth note\textsuperscript{19}.
By reversing the position of the oxygen function so that it adopts the equatorial position (Fig. and ), the molecules lose practically all their odor. In components derived from cis-decalin a camphor-like odor predominates. The two epimeric\textsuperscript{1, 16} 1-endo-cyclohexanc-3-ols are practically odorless\textsuperscript{20}.

Apparently the receptor also accepts that part of a \(-\)orbital which is arranged on the same side as the axial substituent in the 2- or 4-position respectively. This is the case with the double bond in distinctly amergis-like odorant, \(\text{\textsuperscript{21}}\)-ambrinol\textsuperscript{21}, and with the ketone derived from and .
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