A NOTE ON PARACHOR AND RESONANCE

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No work seems to have been done concerning the relation between parachor and resonance structures of molecules.

Theory of resonance requires that the potential energy of the combination of various possibilties should have a solution with minimum potential energy, so as to give a stability to the molecule. It follows therefore that interchangeable electrons should pass more time in the vicinity of the nuclei, for then alone the potential energy can tend to be minimum. It may therefore be stated that a molecule tends to contract so as to have minimum potential energy or the molar volume, or parachor must tend to decrease. Obviously only such resonance structures of a molecule will be possible as will have parachor values not very different from one another, since resonance requires that the various structures should not have much variation in their potential energies. Resonance therefore from the point of view of parachor requires that (i) the various electronic configurations should have the same or practically the same parachor, and (ii) there should be a tendency to contract and hence the observed parachor should be smaller than the calculated one.

It is interesting to observe that the structural parachor of a triple bond 46.2 is practically double of the value 23.2 for a double bond. Similarly the value of parachor of a double bond is exactly twice the parachor for a four-membered ring. These results are not accidental but highly significant. They satisfy the parachor condition(i) for the resonance to occur.

Further, in conjunction with electron diffraction results, they satisfy the condition (ii), since the bond distance decreases as we pass from single covalent bond to double and triple bond provided that the bond distance between the same two atoms is considered. If this significance were realised earlier, parachor results could have been used to predict the principle of resonance.

The structure of carbon suboxide, C_3O_2, can be represented as

$$O = C - C - C = O.$$

Hence, according to above parachor consideration, two double bonds can resonate with a triple bond and a single bond, and hence may have the resonating structures :

$$\overset{+}{O} = C - C \equiv C - \overset{-}{O} \quad \text{and} \quad \overset{-}{O} - C \equiv C - C \equiv \overset{+}{O}$$

This is confirmed from electron diffraction method, since observed carbon to carbon distance 1.30Å and carbon to oxygen distance 1.20Å are shorter than the usual interatomic distances required for a double bond.

Similarly carbon dioxide $O-C-O$ may have the resonance structure $\bar{O}-C\equiv\overset{+}{O}$ and $\overset{+}{O}\equiv C-\bar{O}$. The electron diffraction results indicate $C-O$ distance equal to 1.15Å. The observed value of parachor 77.5 is smaller than the calculated one 91.2, as required by the hypothesis.

The structure of nitric oxide is best represented as $\bar{N}-\overset{+}{N}-O$ (Bailey and Cassie, *Phys. Rev.*, 1932, *ii*, 39, 534). It may therefore have the resonating structure $N\equiv\overset{+}{N}-\bar{O}$. The zero dipole moment of the molecule and electron diffraction confirm this.

The observed parachor 8.1.1 is smaller than the calculated value 91.1, as required by our hypothesis.

The structure of hydrazoic acid shows that resonance between the structures $H-N\leftarrow N\equiv N$ and $H-N\overset{-}{\underset{+}{\rightarrow}}N$ and therefore fulfills the parachor conditions for the existence of resonance. The dipole moment of N_3H is very small (Shomaker and Spurrs, *J. Amer. Chem. Soc.*, 1942, 64, 1184). Azido grouping includes the resonance forms $-N-N\overset{-}{\underset{+}{\rightarrow}}N$ and $-N\leftarrow N\equiv N$ and this is confirmed from small dipole moment of azides (Bergman and Schutz, *Nature*, 1931, 123, 1077) and from interatomic distances and the heat of formation (Roth and Muller, *Ber.*, 1929, 62, 1190). The parachor value for $-N_3$ group is found to be 77.2 (Lindman and Thiele, *Ber.*, 1928, 61,1529 ; 1930, 63,702) and apparently corresponds to the structure

$$-N\overset{\diagup N}{\underset{\diagdown N}{\vert}}\quad(P-77.4).$$
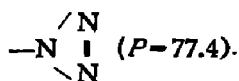
The calculated value for the resonating structures $-N-N\overset{-}{\underset{+}{\rightarrow}}N$ and $N\leftarrow N\equiv N$ is 82.3. Our hypothesis can now explain why the observed value of $-N_3$ is less than 82.3. It is due to resonance between the structures—$N-N\overset{-}{\underset{+}{\rightarrow}}N$ and $-N\leftarrow N\equiv N$, and not due to the cyclic structure as suggested by Lindmann and Thiele (*loc. cit.*).

Aliphatic diazo compounds have the resonance structure $R_2C-N\rightarrow N$ and $R_2C\leftarrow N\equiv N$ which is suggested by electron diffraction measurements. However, the parachor shows cyclic structure (Lindmann and Thiele, *loc. cit.*). The low values according to our hypothesis are due to resonance between two straight chain structures and not due to cyclic structure.

The above example clearly shows the significance of the fact that the parachor value of two double bonds is equal to that of a triple bond. Our hypothesis also explains why the observed parachors should be lower than the calculated ones. The results otherwise apparently confirm the structures not supported by dipole moment and electron diffraction measurements.

Carbon bisulphide, like carbon dioxide, should show resonance between the structures $\bar{S}-C\equiv\overset{+}{S}$, $S-C-S$ and $\overset{+}{S}\equiv C-\bar{S}$ for the same reason. The observed parachor of CS_2 144, is again less than the calculated one 148.

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