

anticyclonic cell. This may perhaps account for some of the rain in the extreme south Peninsula when a southern depression is passing fairly near the equator.<sup>7</sup>

The 'pulses' or low pressure areas that travel from the east to feed the southern depression are not entirely unaffected by the secondary of the western disturbances over India. The western disturbance might 'pull' the low pressure area towards it and delay and occasionally prevent its crossing into the southern hemisphere. Whether the 'pulse' or low pressure area would be pulled towards the low of the western disturbance or to the southern depression depends very much on the relative intensities and positions of the tropical and extra-tropical depressions. The non-crossing of the 'pulse' to the southern hemisphere would create a 'break' in the monsoon there, weaken the depression and might sometimes kill or allow the depression to recurve.<sup>8</sup>

In the event of the western disturbance 'pulling' the low pressure area from the east to west even temporarily, the anticyclonic cell would once again be developing. The stream QSD which leaves the easterlies PQ is gaining in latitude and sometimes would cause weather; to the west of the anticyclonic cell there could be weather due to latitudinal convergence. But if it happens that the low pressure area or 'pulse' is not allowed to cross the equator at all, then there would be a general flow of the stream PQ along SD. In such an event, the resulting convergence would be more pronounced and the rainfall due to the secondary of the particular western disturbance which gets this feed would be greater than usual.<sup>9</sup> Such a contingency (the 'pulse' or the low pressure area not crossing to the southern hemisphere) can arise if the southern depression was filling up or recurved to an easterly direction.

On the other side of the developing anticyclonic cell CR, there would again be stability in the air along the region and the easterly side would be dry. (Rao Bahadur M. G. Subramanyam used to mention a belief held in Rajputana that there would be no rain in North Rajputana in winter so long as there was rain in S.E. Madras, and it is likely that the above is an explanation.)

Hence it follows:

(1) When there is a cyclonic storm in the

South Indian Ocean moving from east to west and it is expected to continue strong or intensify and expected to retain a westward motion, it is safe to tone down the amount of rain due to a western disturbance in Upper India (the longitudinal separation must not be too much between the cyclonic storm and the western disturbance).

(2) When the southern cyclonic storm in the S. Indian Ocean is expected to fill up or recurve towards an easterly direction and the 'pulses' or low pressure areas from the east continue strong north of the equator, the western disturbance gives more rain than usual.

A similar criteria can be used at other places. When the N.E. Trades (in the northern hemisphere) which have had a sea travel continue to be strong, the extra-tropical depression \*just above that latitude would be more active or less active according as the N.E. Trades feed into or away from the depression. The extreme case of the situation is a recurved tropical cyclonic storm, which can give abundant rain or weather. The cyclonic storm recurves when the equatorial maritime air is cut off and the storm is guided by an extra-tropical depression in a higher latitude. In other words, the recurved depression can be considered as a secondary of the extra-tropical depression, which has had a good N.E. Trades feed. Such a criterion would be particularly useful in the Pacific Ocean.

1. S. L. Malurkar, "Forecasting Weather in and Near India," May 1945, p. 108 2. *ibid.*, pp. 101-04; also Tech. Notes, *Ind. Met. Dept.*, No. 1, p. 3. 3. Forecasting Weather, *loc. cit.*, p. 20. Tech. Notes, *ibid.*, No. 20. 4. Forecasting Weather, *loc. cit.*, pp. 106-07. 5. "Sci. Notes," *Ind. Met. Dept.*, 4, p. 137 *et seq.* 6. Hahn, "Handbook of Climatology," Macmillan & Co., 1908, p. 200. 7. Forecasting Weather, *loc. cit.*, p. 99. 8. *ibid.*, p. 95; and also *Curr. Sci.*, 1946, 15, 11. 9. "Forecasting Weather," *loc. cit.*, p. 111.

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## THE MILLS-NIXON EFFECT

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A GROUP of observations by Mills and Nixon<sup>22</sup> on substitution in the aromatic part of hydrindene led them to postulate a "fixation" of the bonds. Since then several other instances of a similar nature have been reported by other workers.<sup>6,7,12,14</sup> Both experimental and theoretical investigations have been reported and Rangaswami and Seshadri<sup>26</sup> have given a fairly comprehensive account of the experimental side,

The main lines on which the experimental investigations have proceeded make use of one or other substitution reaction in the aromatic part of a mixed system. In drawing conclusions from these observations, however, one cannot ignore the limitations of all interpretations based only on chemical reactions. This is clearly brought out by an analysis of the mechanism of the reactions that have been used. The principal reactions that have been

used are the following: (1) Bromination, (2) Nitration, (3) Ozonolysis, (4) The Claisen Rearrangement, (5) The Fries Reaction, (6) The Gattermann Reaction, (7) Coupling with Diazonium Salts and (8) Condensations in the presence of Aluminium Chloride.

The results of the experimental investigations are summarised in Table I.

obvious that the configuration of the aromatic system in the presence of a polarising field as at the instant of reaction cannot be the same in the absence of such a field.

3. The mechanism of ozonolysis in the case of poly-enes is still far from satisfactorily established. Results based on this reaction cannot, therefore, be considered unequivocal

TABLE I  
*Experimental Evidence of Fixation*

Ring system	Reaction used	Results	Reference
Benzene	3, 4, 5, 8	Bond fixation	Levine and Cole <sup>17</sup> Baker <sup>6</sup>
Naphthalene and Tetralin	4, 7 Halogen reactivity Skraup Synthesis	Evidence both for and against fixation of bonds	Baker and Lothian <sup>7</sup> Claisen <sup>10</sup> Fries <sup>14</sup> Fieser and Lothrop <sup>12</sup> Marckwald <sup>21</sup>
Hydrindene	1, 2, 3, 7	ditto	vanBraun and Grüber <sup>32</sup> Borsche and Bodenstein <sup>9</sup> Arnold and Evans <sup>4</sup> Fieser <sup>11</sup>
Fluorene	1, 2, 4, 5	Little fixation of bonds	Macleish and Campbell <sup>20</sup> Sandin and Evans <sup>28</sup> Anantakrishnan & Hughes <sup>3</sup> Bergmann and Berlin <sup>8</sup> Lothrop <sup>10</sup>
Coumarins and Chromones	4, 5	Bond fixation	Baker and Lothian <sup>7</sup> Limaye
Anthracene	1, 7	Evidence both for and against bond fixation	Fries <sup>14</sup> Fieser and Lothrop <sup>12</sup>
Phenanthrene	4, 7	Bond fixation	Fieser, Young and Newman <sup>13</sup> Smith <sup>31</sup>

Taking the reactions in the order given, the position can be summarised as follows:—

1. The essential feature of bromination is that the reagent is the polarised molecule which behaves as an electrophilic reagent and a bromine atom is transferred as a positive ion with a sextet of electrons. The transition state even in the simple case of benzene involves contributions by seven valence bond structures.<sup>33</sup> A study of the reaction at higher temperatures have shown that the relative amounts of isomeric substitution products vary to a considerable extent.<sup>34</sup> The peroxide effect is another complication in polynuclear systems.<sup>23</sup> Any conclusions based on this reaction can at best be an approximation representing the position under the conditions of the experiment.

2. The usual experimental conditions for nitration conform to the initiation of attack by an electrophilic reagent and the conditions for the influence of groups should be analogous to the first reaction. The principal mechanisms that have been postulated for this reaction involve either an addition of nitric acid to the double bond in the aromatic part<sup>25</sup> or initiation of attack by the nitronium ion  $\text{NO}_2^+$ .<sup>15</sup> Kinetic studies as well as the physical properties of solutions of nitric acid under the usual conditions for the reaction are quite consistent with attack by the nitronium ion. The transition state here should involve an even more complex system than bromination. Further, it is

evidence for bond fixation.

4. The migrations of groups to the ortho-position have been used to a considerable extent. The Claisen rearrangement appears to have been used not a little because of the apparent absence of catalytic influences. The undesirable side reactions in the case of ethers of higher boiling point and the better yields with reduced polymerisation during rearrangement when basic solvents are used indicate the complex nature of the problem. The distinct differences noticeable between rearrangements involving the allyl group and of alkyl groups bring out the special features of the allyl group which should be taken into account in using this reaction as evidence for bond-fixation. The para rearrangement seems to require an intermolecular mechanism. Further investigation is clearly needed before one can consider the interpretations as a correct picture. Subject to this limitation, the reaction gives us an indication that bond-orders in the aromatic part of the mixed system or in a substituted benzene are probably not the same in the six-membered ring.

5. The Fries reaction differs from 4 in that the migrating group is an acyl, and definitely requires a catalyst. The relative unreliability of this reaction as a criterion for bond fixation is readily seen from the fact that the nature of the product is dependent on the structure of the ester, the temperature of the reaction, the solvent used and the proportion of the

catalyst used.<sup>1</sup> Existing data are inadequate in fixing a single mechanism; some of the mechanisms that have been proposed treat the reaction as an intermolecular one while others make it out to be an intramolecular one. The mechanistic uncertainty also reduces the value of this as a criterion for bond fixation.

6. The modified Gattermann reaction has been used in very few cases at best as a confirmatory test and with the meagre data no generalisation is possible.

7. Fieser and co-workers have used the coupling reaction with a number of compounds as a specific reaction for establishing bond fixation. If one can assume that Meyer's mechanism of coupling reactions of the diazonium compounds, is the correct one there is some justification in assuming Fieser's interpretation as a probable correct picture. The mechanism of these reactions has not been taken out of the field of controversy and it is necessary to examine if a different explanation of the observations is not possible. It should be stated, however, that of all the chemical evidence adduced in favour of the concept of bond-fixation this reaction is the one with the maximum degree of consistency.

8. These condensation reactions are of too complex a nature to be of much significance for diagnostic purposes at present.

In addition to these reactions physical measurements have also been pressed into service to elucidate the problem under discussion. These include dipole moments,<sup>30</sup> dissociation constants of acids,<sup>4</sup> oxidation-reduction potentials<sup>5</sup> and measurements of bond distances.<sup>10</sup> The first three have been used essentially as methods of comparative study and the results have not turned out to be very conclusive. The measurement of bond distances has not been very helpful either and the values obtained have been generally against any fixation of the double bonds in a specified position.

Before discussing the experimental facts, it is necessary to consider the theoretical treatment of the problem. Two different approaches have been made, one by Pauling and Sutton<sup>24</sup> and the other by Longuet-Higgins and Coulson.<sup>18</sup> Both treat only the specific example of hydrindene and the final results are quite different. The concept of Mills and Nixon<sup>22</sup> that the angles between two single bonds in benzene are different from that between the two double bonds which formed the basis of their suggestion of bond fixation is to some extent at the background of the treatment by the earlier authors. In setting up the secular equation for the wave-functions, Pauling and Sutton ignore the excited structures and consider only the relative contribution of the Kekule forms, the matrix elements including the angle between the ortho-valencies and a bending force constant. The secular equation is solved by assuming that the value of the bending force constant for the C-C bond is the same as that of the C-H bond in HCN and a ratio of the coefficients of the two Kekule structures is calculated to be about 1.05. Using this value, the ratio of the rates of substitution in positions 4 and 6 in hydrindene is derived and the values of the yield are found to be in accord with the experimental observations of Mills. (*loc. cit.*)

Longuet-Higgins and Coulson treat the prob-

lem by the method of molecular orbitals. A fundamental difference in their treatment of the problem lies in the assumptions in evaluating valence angles and bond forces that all the aromatic bonds are of one fixed length, all other carbon-carbon bonds are of a different fixed length, and the energy to form the valence angle at a trigonal carbon is the same whether the linked atoms are carbon or hydrogen. The total energy of the electrons is calculated by the method of Lennard Jones and the resonance integral is obtained as a function of the bond lengths and the force constants of the single and double carbon-carbon bonds. In the absence of standard values of the angular deformation constants needed in the calculations of the stresses involved, the value has been calculated assuming the assignment of the frequency in the propane molecule and treating the system as a non-linear triatomic molecule XY<sub>2</sub>. In a similar manner, the deformation constant for a trigonal carbon has been obtained by a comparison of the bending frequency of propane with that of propylene. A result of the analysis by these authors lead to the observation: "Hence we must abandon the idea that the 4-bond in hydrindene is of a higher order than the 3-bonds and look elsewhere for an explanation of the greater reactivity of the 6- than 4-position in hydroxy hydrindene."

It is interesting to recall here the difficulty in reconciling the electron diffraction results of Kossiakoff and Springall<sup>16</sup> with the dipole moment observations of Sidgwick and Springall. It has been found necessary to abandon the hypothesis of the additivity of bond moments and to postulate additional resonance states in order to account for the apparent discrepancies.

Before we can take up the question of a possible explanation for the experimental observations, attention should also be drawn to Baker's observations on chelation which have played not an insignificant part on this subject of bond fixation. The strength of this evidence depends essentially on the unconscious assumption of a covalency of two for hydrogen. When one recognises that the hydrogen bond whether intermolecular or intramolecular is essentially an ionic bond and a chelate ring can be considered as a mobile electron system, this turns out to be of doubtful value in treating any bond system of the type under consideration as a static system. The question again becomes quite an open one.

It is possible to account for the different observations without postulating any bond fixation. Attention has been drawn early in this account to the limitations of each of the reactions that have been used. Any explanation must take into account the nature of the reaction and whether one approaches the problem from the collision theory or the transition state theory, the factors of diagnostic interest in the rate constant equation are the frequency factor and the energy of activation.

The paucity of accurate kinetic data precludes any quantitative analysis but an approximate computation may none-the-less be attempted. The substitution reactions that have been used may be expected to require an energy of activation of the order of 20 kilocalories, the values being different for the