

09.1-03 MOLECULAR DIMENSION OF INDOLE MOIETY: A COMPREHENSIVE STUDY. Birendra Nath Das*, B.N. Lahiri** and Minakshi Ghosh, Dept. of Physics, Presidency College, Calcutta 700073, India.

The crystal structures of indolyl-3-propionic acid (IPA) and indolyl-3-butyric acid (IBA, a planar trans-conformer), homologues of indolyl-3-acetic acid (IAA), a most active plant growth hormone, have been determined from X-ray diffraction by two of the present authors (Acta Cryst. submitted for publication). In connection with the above structure determinations a comprehensive study of the bond lengths and angles found for the indole moiety in more than fifty indole derivatives including that of IPA and IBA is made to visualise the most probable molecular dimension of the indole moiety.

The study of the dimension of the indole moiety as found in different environments showed consistent and definite distortions in the bond lengths and angles. Substitution of hydrogen in the indole moiety has a definite effect on the ring geometry but this effect is independent of the nature of the substituent. The differences between different molecules arise mainly at the point of substitution and hence the most probable molecular dimension of the indole moiety can be predicted (Das, Ph.D. Thesis, Univ. of Calcutta, 1980). The geometry of the indole moiety which differs considerably from that of the individual benzene and pyrrole rings, appears to be due to perturbations occurring both in the sigma and pi electron system of the rings. The general pattern of observed bond lengths is also found in the theoretically calculated indole ring system (SCF-LCAO-PIMO approximation within the Pariser-Parr-Pople formalism; Lahiri, Ph.D. Thesis, Univ. of Calcutta, 1972). This indicates that bond length variations within the indole moiety may be due to the electronic structure of the isolated indole molecule at rest. We are aware that the procedure is open to criticism and a detailed study of the conformation, bond lengths and angles for different substituents is proposed along with theoretical calculations of bond lengths and angles using ab initio methods on model compounds to observe finer details. The ring geometry by X-ray diffraction may also be affected by the effects of thermal motion specially in the case of bond lengths and hence angular values are more reliable. While no consideration is given to the experimental temperatures the molecular dimension is obtained by averaging over the most accurate determinations with comparable precision. The mean experimental dimension of the indole moiety, numbered according to international convention, are as follows with theoretical values in parentheses:

Bonds: 1-2 1.373(1.367), 1-8 1.376(1.375)
(in Å) 2-3 1.362(1.372), 3-9 1.435(1.431)
4-5 1.375(1.387), 4-9 1.401(1.415)
5-6 1.395(1.407), 6-7 1.372(1.388)
7-8 1.393(1.412), 8-9 1.407(1.414)
Angles: 2-1-8 108.8, 1-2-3 110.3, 2-3-9 106.2
(in deg) 3-9-8 107.3, 1-8-9 107.3, 5-4-9 118.7
4-5-6 121.2, 5-6-7 121.5, 6-7-8 117.4
7-8-9 122.1, 4-9-8 119.0, 1-8-9 130.5
3-9-4 133.7

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09.1-04 p-NITROANILINE REVISITED.

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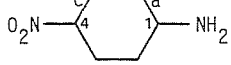
The crystal and molecular structure of p-nitroaniline was studied 20 years ago by Trueblood, Goldish & Donohue (Acta Cryst., 14, 1009 (1961)). Their refinement, based on visually estimated photographic data, led to $R = 0.095$. The geometry obtained indicated that a quinoid form was contributing to the structure; but, curiously, the amino group appeared to interact with the benzene ring to a greater extent than the nitro group.

In view of the fundamental importance of this molecule in the study of through-conjugation (i.e. cooperative interaction between π -donor and π -acceptor substituents) we have carried out a refinement based on accurate counter intensities (Mo $K\alpha$ radiation, 1041 reflections, $R = 0.046$, $\sigma(\text{C-C}) = 0.003 \text{ \AA}$, $\sigma(\text{C-C-C}) = 0.2^\circ$).

The geometry of p-nitroaniline may be compared with those of aniline (a microwave study by Lister et al., J. Mol. Struct., 23, 253 (1974)) and p-nitrobenzoic acid (further refinement of the crystal structure, based on the X-ray data of Colapietro & Domenicano, Acta Cryst., B33, 2240 (1977)). The comparison with p-nitrobenzoic acid (where cooperative interactions between substituents do not occur) is particularly significant since the two molecules were studied by the same technique.

The effects of through-conjugation are very clearly seen throughout the heavy-atom skeleton of the molecule.

The following points deserve special mention:

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- (i) the a bonds, 1.406-1.408 Å, are 0.009-0.011 Å longer than in aniline;
- (ii) the b bonds, 1.365-1.368 Å, are 0.021-0.024 Å shorter than in p-nitrobenzoic acid;
- (iii) the c bonds, 1.391 Å, are 0.008-0.009 Å longer than in p-nitrobenzoic acid;
- (iv) the C-NH₂ bond, 1.356 Å, is 0.046 Å shorter than in aniline;
- (v) the C-NO₂ bond, 1.437 Å, is 0.038 Å shorter than in p-nitrobenzoic acid;
- (vi) the two N-O bonds, 1.228-1.234 Å, are ca 0.01 Å longer than in p-nitrobenzoic acid;
- (vii) the O-N-O angle, 121.8°, is 2.5° smaller than in p-nitrobenzoic acid;
- (viii) the amino group makes an angle of 10.6° with the plane of the benzene ring (the corresponding angle in aniline is 37.5°);
- (ix) the nitro group makes an angle of 1.9° with the plane of the benzene ring (the corresponding angle in p-nitrobenzoic acid is 13.7°);
- (x) the internal angles of the ring at C1 and C4, 118.5° and 120.9° respectively, are both 0.7° less than the values calculated from the empirical angular parameters of Domenicano & Murray-Rust (Tetrahedron Lett., 2283 (1979)), assuming additivity of substituent effects.

It appears that the two substituents are involved to essentially the same extent in the cooperative interaction.