10. Schmidt, N. J., Lennette, E. H., Doleman, J. H. and Hagens, S. J., *Am. J. Hyg.*, 1957, 66, 1.
11. Weller, T. H. and Witton, H. M., *J. Exptl. Med.*, 1958, 108, 869.
12. Churcher, G. M., Sheffield, F. W. and Smith, W., *Brit. J. Exptl. Pathol.*, 1959, 40, 87.
13. Klemperer, H. G. and Pereira, H. G., *Virology*, 1959, 9, 536.
14. Schmidt, N. J. and Lennette, E. H., *Am. J. Hyg.*, 1959. 70, 51.
15. Bucca, M. A.. Casey, H. L. and Winn., J. F., *Proc. Soc. Exptl. Biol. Med.*, 1960, 104, 247.
16. Westwood, J. C. N., Appleyard, G., Taylor-Robinson, D. and Zwartouw, H. T., *Brit. J. Exptl. Pathol.*, 1960, 41, 105.
17. Caunt, A. E., Rondle, C. J. M. and Downie, A. W., *J. Hyg.*, 1961, 59, 249.
18. Schmidt, N. J. and Lennette, E. H., *J. Immunol.*, 1962, 89, 85.
19. Versteeg, J., *Proc. Kon. Ned. Acad. Wet.*, 1963, 66, 157.
20. Schmidt, N. J., Lennette, E. H., Shon, C. W. and Shinomoto. T. T., *Proc. Soc. Exptl. Biol. Med.*, 1964, 116, 144.
21. Andrewes, C. H., *Virology*, 1970, 40, 1070.

## A MOLECULAR ORBITAL TREATMENT OF SOME HALOGEN SUBSTITUTED AMIDES

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ABSTRACT

A Huckel molecular orbital treatment of some halogen substituted formamide, acetamide and benzamide series has been carried out to study the effect of substitutions (Cl, Br, I) on the charge delocalization in these molecules. The net charges on carbon, oxygen, nitrogen and halogen atoms and the bond orders of the C = O and C — N bonds have been calculated and the results are discussed. The barrier heights for the internal rotation about the C — N bond and resonance energies are also calculated.

### INTRODUCTION

IT is well known that in amide molecules, no single valence bond structure is consistent with all their properties. This is due to the delocalization of the carbonyl π-electrons and lone pair electrons of nitrogen, resulting in the double bond character of the C — N bond[1-5]. Infrared, Raman and NMR Spectroscopic studies of halogen substituted amides have been carried out by Petterson[6], Laches[7] and recently by Deklein[8,9] and Devia[10]. In the present work, the authors have attempted to make a systematic study of electronic charges on O, C, N and halogen atoms and bond orders of C = O and C — N groups to study the charge delocalization due to different substitutions.

### METHOD OF CALCULATION, RESULTS AND DISCUSSION

The Huckel molecular secular determinant of a representative secondary amide is as shown in Fig. 1. Where the $\alpha$ and $\beta$ are the coulomb and resonance integrals respectively of the atoms O, C, N and the substituent to $R_1$ and X.

The secular determinant was solved using a CDC 3600 computer. The solution of the determinants provides the eigen values and eigen functions of the energy levels. Treating this as a six electron problem, the three lowest levels are taken as filled.

The mobile bond orders and the π-electronic charge defined in the usual way were determined. The net charge was determined as the difference between the charge the atoms would have in the absence of delocalization and its actual calculated electronic charge. A positive sign denotes a deficit and a negative sign an excess of electronic charge. T. Yanezawa *et al.*[11] parameters are used in the calculations.

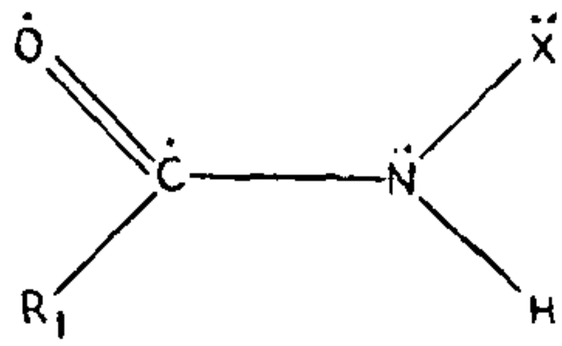


FIG. 1

The results are tabulated in Tables I and II. As the aim of the present investigation is to study the relative delocalization of the charge due to the different halogen substitutions, the HMO method is used. This method is well suited for comparative study and the results depend upon the choice of the parameters of the coulomb and the resonance integrals,

In halogen substituted amides the net charge on oxygen increases from formamide to acetamide and acetamide to benzamide whereas the corresponding deficit in charge is decreasing on carbon atom. On the other hand the net charge on nitrogen atom shows an increase in the deficit of the charge. In formamide series the net charge on oxygen is increasing as we go from Iodine to Bromine to Chlorine. But in acetamide series the net charge on oxygen is decreasing as we go from iodine to bromine to chlorine. Compared to chloro and bromo benzamide the iodobenzamide has less charge on oxygen, the variation of charge on oxygen being small.

The charge on nitrogen atom in all the three series (*i.e.*) formamide, acetamide and benzamide show less deficit as we go from Chloro to Bromo to Iodo substitutions. These results indicate that a relatively large delocalization is taking place from nitrogen lone pair electrons to carbonyl bond.

The bond orders of the C = O and C – N bonds as obtained by the authors in these studies are of the same order as obtained by Morris *et al.*[1] in case of primary amides like formamide and acetamide. The carbonyl bond orders in all halogen substituted amides show decreasing tendency from formamide to benzamide. The carbonyl bond order in formamide shows an increase from chloro to bromo to iodo substituted amides. Similar variations are observed in the case of acetamide and benzamide series. The C – N bond order in formamide series shows a decrease from chloro to bromo to iodo. Similar variation is found in acetamide and benzamide series.

In Table II, the calculated bond orders of C = O bonds and corresponding stretching frequencies[8] are presented. The net charge on nitrogen atom and N – H stretching frequencies[8] are correlated. The more positive the nitrogen atom means, the lesser the strength of the N–H bond and hence a decrease in the N – H stretching frequency.

**Table I**

*Net charges of oxygen, carbon, nitrogen and halogen atoms and bond orders of C = O and C – N bonds in halogen substituted amides*

| | Net Charges on | | | | Bond Orders | |
|---|---|---|---|---|---|---|
| | Oxygen | Carbon | Nitrogen | Halogen | C – O | C – N |
| 1. Chloro Formamide .. | −0·729 | +0·344 | +0·359 | +0·026 | 1·603 | 1·695 |
| Chloro Acetamide .. | −0·764 | +0·242 | +0·663 | +0·118 | 1·519 | 1·693 |
| Chloro Benzamide .. | −0·771 | +0·238 | +0·701 | +0·134 | 1·516 | 1·685 |
| 2. Bromo Formamide .. | −0·728 | +0·348 | +0·353 | +0·027 | 1·606 | 1·690 |
| Bromo Acetamide .. | −0·765 | +0·230 | +0 654 | +0·150 | 1·521 | 1·685 |
| Bromo Benzamide .. | −0·772 | +0·226 | +0 690 | +0·174 | 1·514 | 1·675 |
| 3. Iodo Formamide .. | −0·723 | +0·365 | +0·345 | +0·013 | 1·612 | 1·683 |
| Iodo Acetamide .. | −0·785 | +0·242 | +0·625 | +0·148 | 1·530 | 1·683 |
| Iodo Benzamide .. | −0·765 | +0·237 | +0·658 | +0·286 | 1·522 | 1·675 |

**Table II**

*Frequencies and bond orders of carbonyl bond in halogen substituted acetamide and benzamide*

| Amide | ν(C = O) | Bond order | Charge on N atom | N–H stretching frequency |
|---|---|---|---|---|
| N-Cl Acetamide | 1,728 | 1·519 | +0·663 | 3,420 |
| N-Cl Benzamide | 1,714 | 1·516 | +0·701 | 3,416 |
| N-Br Acetamide | 1,717 | 1·521 | 0·654 | 3,422 |
| N-Br Benzamide | 1,704 | 1·514 | 0·690 | 3,418 |

The barriers to internal rotation about C – N bond of these amides are calculated using the concept of *cis-trans* localization energy. In order to undergo *cis-trans* isomerization the system must

pass through a stage in which N–X π-electrons on one hand and carbonyl π-electrons on other hand are uncoupled. This stage may be taken as transition stage and the energy needed to bring the

pronounced in N-iodo amides compared to those of the corresponding N-chloroamides.

The resonance energies are calculated as the difference between the total energy of delocalized

TABLE III

*The pielectronic energy of N-halogen substituted amide and its fragments along with calculated barrier to internal rotation and C–N* bond order

| Amide | Electronic energy | electronic energy of the fragments | | Barrier to internal rotation in $\beta$ | C—N bond order | Resonance energy in $\beta$ |
|---|---|---|---|---|---|---|
| | | Structure | Structure | | | |
| 1. N-Chloroformamide | $6\alpha+11\cdot903\beta$ | $2\alpha+5\cdot464\beta$ | $4\alpha+5\cdot600\beta$ | 0·839 | 1·695 | 0·839 |
| N-Chloroacetamide | $6\alpha+12\cdot260\beta$ | $2\alpha+5\cdot616\beta$ | $4\alpha+5\cdot600\beta$ | 1·044 | 1·683 | 1·196 |
| N-Chlorobenzamide | $6\alpha+12\cdot287\beta$ | $2\alpha+5\cdot621\beta$ | $4\alpha+5\cdot600\beta$ | 1·066 | 1·685 | 1·223 |
| 2. N-Bromoformamide | $6\alpha+11\cdot094\beta$ | $2\alpha+5\cdot464\beta$ | $4\alpha+4\cdot800\beta$ | 0·830 | 1·690 | 0·830 |
| N-Bromoacetamide | $6\alpha+11\cdot456\beta$ | $2\alpha+5\cdot616\beta$ | $4\alpha+4\cdot800\beta$ | 1·040 | 1·685 | 1·192 |
| N-Bromobenzamide | $6\alpha+11\cdot486\beta$ | $2\alpha+5\cdot621\beta$ | $4\alpha+4\cdot800\beta$ | 1·065 | 1·675 | 1·222 |
| 3. N-Iodoformamide | $6\alpha+10\cdot681\beta$ | $2\alpha+5\cdot464\beta$ | $4\alpha+4\cdot400\beta$ | 0·817 | 1·683 | 0·817 |
| N-Iodoacetamide | $6\alpha+11\cdot028\beta$ | $2\alpha+5\cdot616\beta$ | $4\alpha+4\cdot400\beta$ | 1·012 | 1·683 | 1·164 |
| N-Iodobenzamide | $6\alpha+11\cdot056\beta$ | $2\alpha+5\cdot621\beta$ | $4\alpha+4\cdot400\beta$ | 1·035 | 1·675 | 1·192 |

amide system to this particular stage as a measure of barrier. Since uncoupled π-electrons remain conjugated to molecular fragment on its side, the representation of transition stage involves two radical fragments (structure II and III).

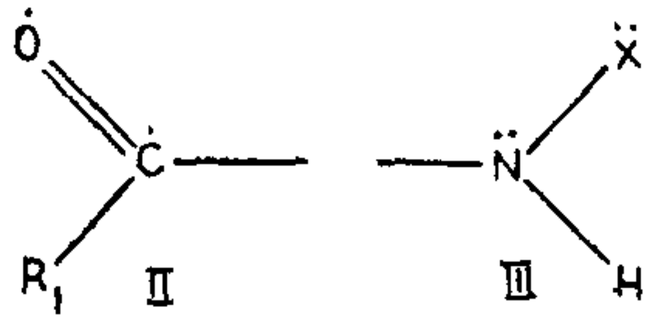


FIG. 2.

Thus the energy which must be spent to bring the molecule in this state is the difference between the energy of whole conjugated molecule and sum of the energies of fragments. This then is a measure of barrier to internal rotation.

The π-electronic energy of whole molecule, of fragments, barrier to internal rotation and C–N bond orders are presented in Table III. It is seen from the observations in Table III that the height of the potential is less in formamide series compared to that in the corresponding molecules of acetamide and benzamide series. The barrier to rotation decreases from N-chloro, to N-bromo and N-iodo amides in each series and this is very

system and the energy the system would have if carbonyl double bond, and nitrogen and halogen lone pairs were localized. The results of the calculations are also included in Table III. The resonance energy increases in all halogen substituted amides from formamide to acetamide to benzamide. On the other hand in all the formamide, acetamide and benzamide series the resonance energy decreases as we go from chlorine to bromine to iodine substitutions at the N-position.

1. Morris, R. E. and Orville Thomas, W. J., *J. Mol. Spect.*, 1961, 6, 572.
2. Cannon, C. G., *J. Chem. Phys.*, 1956, 24, 491.
3. —, *Michrochim. Acta*, 1955, 2, 555.
4. Venkata Chalapathi, V. and Venkata Ramiah, K., *J. Mol. Spect.*, 1968, 26, 444.
5. Venkata Ramiah, K. and Venkata Chalapathi, V., *Curr. Sci.*, 1971, 40, 363.
6. Petterson, R. C. *et al.*, *J. Org. Chem.*, 1960, 25, 1595.
7. Laches, J. R., *et al.*, *J. Am. Chem. Soc.*, 1952, 74, 5578.
8. Deklein, L. J. and Plesman, A. R., *Spectrochim. Acta*, 1972, 28 A, 673.
9. —, *Ibid.*, 1972, 28 A, 673.
10. Jorge, E. Devia and James, C. Carter, *Ibid.*, 1973, 29 A, 613.
11. Yonezava, T. *et al.*, *Electronic Absorption Spectra and Geometry of Organic Molecules*, Academic Press, Inc., N.Y., Suzuki H., 1967, p. 187.