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# DEPENDENCE OF RADICAL ANION STABILITY ON CRYSTAL STRUCTURE

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Abstract An INDO calculation using the RHF/CI method indicates that the minimum energy conformation of the $[XCH_2CONH_2]^-$ radical anions where X = F, Cl, Br and I occurs if the C-X bond is located in a direction approximately normal to the CON plane. It has been experimentally shown that for these radical anions to be observed in single crystals by EPR methods, the molecular precursor should not exist in the energy maximum conformation for radical anions or else spontaneous elimination of $X^-$ occurs upon electron attachment. This suggests that $F^-$ elimination from dopants (e.g. $AsF_5$) used in the formation of conducting polymers may be a general phenomenon if the anion is formed from a maximum energy configuration.

## INTRODUCTION

Recently,[1] there has been considerable interest in the preparation of conducting polymers either by acceptor or donor doping of various polymers such as polyacetylene, poly (p-phenylene) and poly(p-phenylene sulfide). Acceptor doping[1,2] by $AsF_5$ is of considerable interest since its use produces some of the highest conducting polymers. Unfortunately, little is known about the actual chemistry that occurs during the doping process, because of the difficulty in measuring the intermediates that are formed, although $AsF_6^-$ and HF are presumably formed as well as other species. In this paper, we report an INDO molecular orbital and crystallographic study of the radical anion stability of $[FCH_2CONH_2]^-$ in single crystals of $CFH_2CONH_2$. Unfortunately, there are few fluorinated single crystal systems that closely mimic the actual reactions occurring in doped polymers. However, this crystal allows us to examine a system where HF is produced and an electron attachment to a fluorine occurs.

It has been shown that the radical anion $^-ICH_2CONH_2$ is stable[3-5] at 77 K in the dark in X-ray irradiated iodoacetamide crystals, yet the radical anion $^-FCH_2CONH_2$ is not stable in the dark even at 3 K in X-ray irradiated fluoroacetamide[6] crystals. In contrast all radical anions of the type $[XCF_2CONH_2]^-$ where X = F, Cl, Br are stable at 77 K in the dark in X-ray irradiated crystals of the parent compounds.[7-9]

In this paper it will be shown by an INDO molecular orbital calculation using the RHF/CI method, that the instability of the $[FCH_2CONH]^-$ radical is due to the molecular precursor residing in an energy maximum conformation for radical anion formation.

## EXPERIMENTAL

An INDO molecular orbital calculation using the RHF/CI method, as applied by Oloff and Hütterman,[10] was used to determine the most stable geometrical configuration of $[XCH_2CONH_2]^-$ where X = F, Cl, Br and I. The bond lengths and angles when X = Cl, Br and I were obtained from the crystal structure of $CBrF_2CONH_2$,[11] except for the C-H (standard bond lengths) and C-X bond lengths. A rearranged conformation of the $CXF_2$ group found to give the best agreement between the calculated and experimental coupling constants[9] for $[CBrF_2CONH_2]^-$ was used for the calculation of the coupling constants for $[CXH_2CONH_2]$ where X = Cl, Br and I. In this rearranged conformation, the dihedral angle between the C-X bond and the normal to the CON plane equals 0°. In addition, the $C_2C_1$-X angle equaled 90°. The crystallographic angles and lengths for $FCH_2CONH_2$[12] were used to calculate the minimum energy configuration for $^-FCH_2CONH_2$. Only the s and p basis functions for the different atoms were used. Incorporation of d-orbital basis functions placed unacceptably too high a spin density on the halogen and, in general, gave poor agreement with the experimental spin density.

## RESULTS AND DISCUSSION

Variation of the $FC_1C_2O$ dihedral angle resulted in an energy minimum for $[FCH_2CONH_2]^-$ when $\theta = 0°$, where $\theta$ is the angle between the normal to the CON plane and the direction of the C-F bond. The INDO barrier to rotation about the $C_1$-$C_2$ bond is 11.3 kcal/mole. The most stable conformation is given in Figure 1. No attempt was made

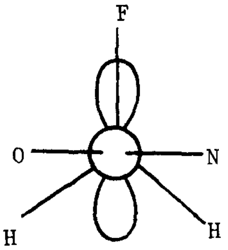


Figure 1. The most stable conformation of $[FCH_2CONH_2]^-$

to determine whether the structure of the CON group was planar. For the $[CF_3CONH_2]^-$ radical, the best fit between the calculated and experimental fluorine couplings was obtained when the CON plane deviated by $\phi = 32^o$ from the planar molecular position determined crystallographically. Since the $[FCH_2CONH_2]^-$ ion has not been experimentally observed,[6] the electron densities reported in Table I were those of the planar configuration.

A variation in the angle $\phi$ for the nonplanarity of the CON plane in $[XCH_2CONH_2]^-$ when X = Cl, Br, and I resulted in an energy minimum when $\phi = 0^o$. The energy minimum for the $XC_1C_2O$ dihedral angle equaled $90^o$.

Unfortunately, EPR couplings have not been reported for $[BrCH_2CONH_2]^-$ but they have been reported for $[ICH_2CONH_2]^-$.[3-5] A variation of the C-I bond length from the typical C-I molecular bond length of 2.17 Å to 2.7 Å showed that an improved fit to the observed iodine coupling constants occurred when the C-I bond length equaled 2.50 Å, suggesting that the C-Cl, C-Br and C-I bonds in the respective molecules may lengthen upon anion formation. The coupling constants calculated from the unpaired spin density listed in Table I for X = I (C-I = 2.50 Å) equals 142.7 Gauss for $a_{iso}(^{127}I)$ and -8.7 Gauss for $a_{iso}(^1H)$. This compares favorably with the experimentally observed coupling of $a_{iso}(^{127}I) = 144.5$ Gauss.[3-5]

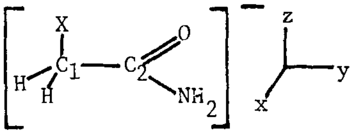
Upon inspection of Table I, it is noted that 80% of the unpaired electron density in $[CFH_2CONH_2]^-$ is located on $C_2$ and O, largely in the $P_z$ orbital, with a small unpaired spin

Table I. INDO Unpaired Spin Densities Calculated for the Minimum Energy Configuration of $[XCH_2CONH_2]^-$.

| X= | X |  | $C_1$ |  | $C_2$ |  | O |  | N |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | $\rho_s$ | $\rho_p^a$ | $\rho_s$ | $\rho_p^a$ | $\rho_s$ | $\rho_p^a$ | $\rho_s$ | $\rho_p^a$ | $\rho_s$ | $\rho_p^a$ |
| F (C-F = 1.406Å) | 0.01 | 0.10 | 0.01 | -0.02 | 0.02 | 0.46 | 0.008 | 0.34 | 0.01 | 0.060 |
| Cl (C-Cl = 1.780) | 0.04 | $0.27^b$ | 0.10 | $0.17^b$ | 0.01 | 0.14 | 0.006 | $0.25^b$ | 0.001 | 0.016 |
| Br (C-Br = 1.900) | 0.04 | $0.33^b$ | 0.14 | $0.34^b$ | 0.00 | -0.00 | 0.004 | $0.17^b$ | 0.00 | 0.001 |
| I (C-I = 2.172Å) | 0.04 | $0.34^b$ | 0.14 | $0.41^b$ | -0.003 | -0.03 | 0.003 | $0.14^b$ | 0.00 | -0.003 |
| I (C-I = 2.500Å) | 0.02 | $0.32^b$ | 0.13 | $0.49^b$ | -0.005 | -0.09 | 0.003 | $0.15^b$ | 0.00 | -0.008 |

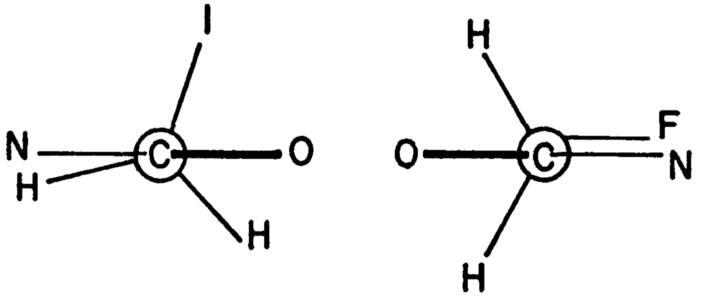
a. $\rho_p$ = sum of the unpaired spin density in the $P_x$, $P_y$, $P_z$ orbitals.

b. A majority of the unpaired density is located in the $P_z$-orbital.



density located in the $P_z$ orbital of F. This would indicate that the lowest energy conformation of the $[FCH_2CONH_2]^-$ radical is predicted to be a π-anion radical. On the other hand, 85% and 96% of the unpaired spin density is located on the C-Br and C-I atoms respectively, with a vast majority residing in the $P_z$ orbitals, indicating that $^-BrCH_2CONH_2$ and $^-ICH_2CONH_2$ are σ*-anion radicals. The unpaired electron density is more evenly distributed in the $[CClH_2CONH_2]^-$ anion radical with 58% on the methyl C and Cl atoms and the remaining on the amide oxygen and carbon. Thus $[CClH_2CONH_2]^-$ represents a radical with a structure intermediate between a π- and σ*- type anion radical.

The interesting and most important point is that the minimum energy conformation for both π- and σ*- radical anions occurs when the $XC_1C_2O$ dihedral angle equals 90°. This is important when considering the crystal structures of $FCH_2CONH_2$ and $ICH_2CONH_2$. The crystallographic dihedral angle $FC_1C_2N$ equals 0° while the dihedral angle $IC_1C_2O$ equals 67.3°. The exact conformation is given in Figure 2.



I

II

Figure 2. The relative experimental conformations of $ICH_2CONH_2$(I) and $FCH_2CONH_2$(II).

The C-I bond in crystals of $ICH_2CONH_2$ occurs close to the direction needed for the minimum energy conformation required for the formation of $^-ICH_2CONH_2$. On the other hand, the C-F bond in crystals of $FCH_2CONH_2$ is locked in an energy maximum for the formation of $^-FCH_2CONH_2$ by the presence of an amide proton located 2.28 Å from the fluorine atom.[12] This packing arrangement gives rise to a strong attraction that prevents rotation of the $CFH_2$ group in the crystal. It is thus no surprise that there is great difficulty in isolating the $^-FCH_2CONH_2$ anion since spontaneous dissociation into the neutral radical $CH_2CONH_2$ and $F^-$ occurs instead. The crystal structure of $CFH_2CONH_2$ is made up of layers of $CFH_2CONH_2$ molecules which also promote an alternative reaction. The layering places the fluorine atom directly above the methyl hydrogen of the adjacent molecule located along the c axis. Thus elimination of $H^+$ from $[CFH_2CONH_2]^+$ by migration of the $H^+$ along the c crystal direction results in HF and in the formation of the radical pair[13] $H_2NCO\dot{C}H_2$.... $F\dot{C}HCONH_2$. This is yet another reason for the absence of any $[CFH_2CONH_2]^-$. In conclusion, $F^-$ elimination may be preferred in acceptor doping of polymers, if the conformation of the fluorinated dopant lies at the energy maximum for anion formation. HF production appears to be favored if a layered structure exists in which the fluorinated acceptor anion is found in one layer while the protonated cation occurs in the adjacent layer.

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## REFERENCES

1. R. H. Baughman, J. L. Bredas, R. R. Chance, R. L. Elsenbaumer, and L. W. Shacklette, Chem. Rev.,82, 209 (1982) and references cited therein.
2. L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, Synthetic Metals, 1, 307(1979).
3. R. F. Picone and M. T. Rogers, J. Magn. Res., 14, 279 (1974).
4. R. J. Booth, S. P. Mishra, G. W. Neilson, and M. C. R. Symons, Tetrahedron Lett., 34 2949 (1975).
5. P-O. Samskog, L. D. Kispert, and B. Kalyanaraman, Chem. Soc. Faraday 2, 1984 in press.
6. P-O. Samskog, L. D. Kispert, and D. P. Murray, Chem. Phys. Letters, 101, 106 (1983).
7. P-O. Samskog and L. D. Kispert, J. Chem. Phys., 78 2129 (1983).
8. L. D. Kispert, R. Reeves, and T. C. S. Chen, J. Chem. Soc. Faraday Trans. 2, 74, 871 (1978).
9. P-O. Samskog and L. D. Kispert, J. Phys. Chem. 1984 in press.
10. H. Oloff and J. Hütterman, J. Magn. Res., 40, 415 (1980).
11. B. Kalyanaraman, L. D. Kispert, and J. L. Atwood, Acta Cryst., B 34, 1131 (1978).
12. D. O. Hughes and R. W. Small, Acta Cryst., 15, 933 (1962).
13. M. Iwasaki and K. Toriyama, J. Chem. Phys., 46, 4693 (1967).