Pak. J. Agri. Sci., Vol. 21 (3-4) 1984

CRYSTAL STRUCTURE OF (INDOLYL - 3) PHENYL IODONIUM TRIFLUORO ACETATE

Fiyyaz A. Chughtai* and Valadimir A. Budylin**

ABSTRACT

Calculations based on X-ray projection studies revealed that (Indolyl-3) phenyl iodonium trifluoroacetate is a T-shaped molecule. However, if two nonbonded electron pairs on iodine are taken into account, the molecule would have trigonal—bipyramidal structure, the indolyl ring and two lone pairs on the equatorial position, the phenyl ring and trifluoroacetate ion at the apices.

INTRODUCTION

X-ray data are available for diphenyl iodonium chloride (Khotsyanova, 1957) iodide (Khotsyanova, 1975), bromide (Khotsyanova, 1976) and fluoroborate (Struchkov and Khotsyanova, 1960). The first three are isomorphus while fluoroborate is purely an ionic salt. These molecules have T-shaped structure. Chloride, bromide and iodide crystals belong to the same space group C_2/c, and contain eight molecules per unit cell, whereas, fluoroborate crystal belongs to space group P_2/C and contains four molecules per unit cell. However, iodonium salts containing the indolyl group as a ligand have not been reported so far.

Interested in the chemistry of such types of iodonium ion, the crystal structure of (Indolyl-3) phenyl iodonium trifluoroacetate is reported herein.

MATERIALS AND METHODS

General : Melting points were taken in capillary tubes. In this connection, it was found that the iodonium salts decomposed near their melting points which depended strongly on the duration of heating. Therefore, after an approximate m.p. had been taken, a new sample was introduced at about 10°C

* Department of Chemistry, University of Agriculture, Faisalabad.
**Faculty of Chemistry, Moscow State University, Moscow, USSR.

below this point and thon the temperature was slowly raised. A Perkin-Elmer 257 IR spectrometer was used for IR spectra. Elemental analyses were performed by the Department of Analytical Chemistry at the Moscow State University, USSR.

Iodosobenzene diacetate : This salt (m.p. 157-158°C) was prepared by the the method of Pausacker (1953).

(*Indolyl-3*) *phenyl iodonium betain* : This was synthesized according to a procedure of Chughtai *et al.* (1981).

(*Indolyl-3*) *phenyl iodonium trifluoroacetate* : To a suspension of 12.76gm (0.04 mol) of (Indolyl-3) phenyl iodonium betain in 20 ml of ethanol was added dropwise 4.56 gm (0.04 mol, 3.1 ml) trifluoroacetic acid with stirring below-5°C. Stirring was continued for an additional 15 minutes. To the reaction mixture, was added 300 ml pure ether (free from peroxide) and allowed to stand overnight in the freezer. The solvent was removed by filtration. The colourless crystals were washed with small amount of ether and dried under reduced pressure, giving 13 9 gm (80%) of (Indolyl-3) phenyl iodonium trifluoroacetate m.p. 126-126°C (decomp). This salt was recrystallized from methanol-ether to to yield colourless crytals, m. p- 127-128°C (decomp.).
(found : C, 43 6; H, 2.5%; $C_{16}H_{11}F_3INO_2$; required : C, 44.3; H, 2.6%).

X-ray analysis of the salt : Very thin crystal of the title compound was used for X-ray measurements. Different cell parameters were measured with automatic four circle differactometer syntex $P2_1$. Since iodonium salt, under investigation, decomposed at room temperature during X-ray analysis, therefore, investigations were carried out at-120°C using low temperature device CT-1.

RESULTS AND DISCUSSION

(Indolyl-3) phenyl iodonium trifluoroacetate (I) was synthesized from phenyliodoso acetate and indole in methanolic potassium hydroxide with subsequent treatment of trifluoroacetic acid.

A thin crystal of the iodonium salt was then examined for X-ray analy-

sis. The crystallographic data are given in Table 1. The atomic numbering scheme and bond lengths are shown in molecular structure representation of the salt in Fig. 1.

Table 1. *Crystallographic data of the title compound*

Formula		=	$C_{16}H_{11}F_3INO_2$
Formula weight	F	=	433
Melting point		=	128°C
Density observed		=	1.89 gm/cm^3
Lattic constants	a	=	9.29 Å, b = 10.26 Å, c = 10.28 Å
	α	=	111.01°, β = 108.66°, γ = 106.83°
Volume of the unit cell	V	=	762.5 A$^{\circ 3}$
Density calculated	d	=	1.886 gm/cm^3 ($d = \frac{1.66z \times F}{V}$)
Formula units/cell	Z	=	2
Bond Lengths	I – O^1	=	2.736 Å, I – C^{10} = 2.12 Å,
	I – C^3	=	2.046 A
Bond angles	C^3 – I – C^{10}	=	98.3°, C^{10} – I – O^1 = 87°,
	C^3 – I – O^1	=	172.2°

X-ray crystallographic studies revealed that the title compound 'I' is triclinic and belongs to space group P_1 containing two molecules per unit cell. The calculated density, 1.886 gm, cm^{-3} agreed with the experimentally determined density, 1.80 gm cm^{-3}. The linear group C_3 Ind (3-carbon at Indol ring The linear group C_3 Ind (3-carbon at Indol ring)-I-O^1 is perpendicular to the other C_{10} Ph (carbon at phenyl ring)-I group making it T-shaped molecule

Ph

(Ind-I-O). This configuration owing to steric hinderance is somewhat distorted, thus C^3 I O^1 = 172.2°, C_3 I C^{10} = 98.3° and C^{10} I O^1 = 87.0° as shown in Fig. 1. Taking into consideration the structural position of the two lone pairs of iodine atom (Phanton-Ligands), the molecule would be slightly distorted trigonal

bipyramidal with indolyl group and the two lone electron pairs occupying the equatorial positions and the phenyl ring and trifluoroacetate ion at the apical positions. Since the equatorial positions are roomier than the axial positions, it is reasonable that a bulkier indolyl group would preferably occupy one of these, rather than a more crowded axial position. Such a trigonal-bipyramidal structure has also been reported for substituted phenyl-2-thienyl-iodonium halide (Yamda and Okawara, 1972).

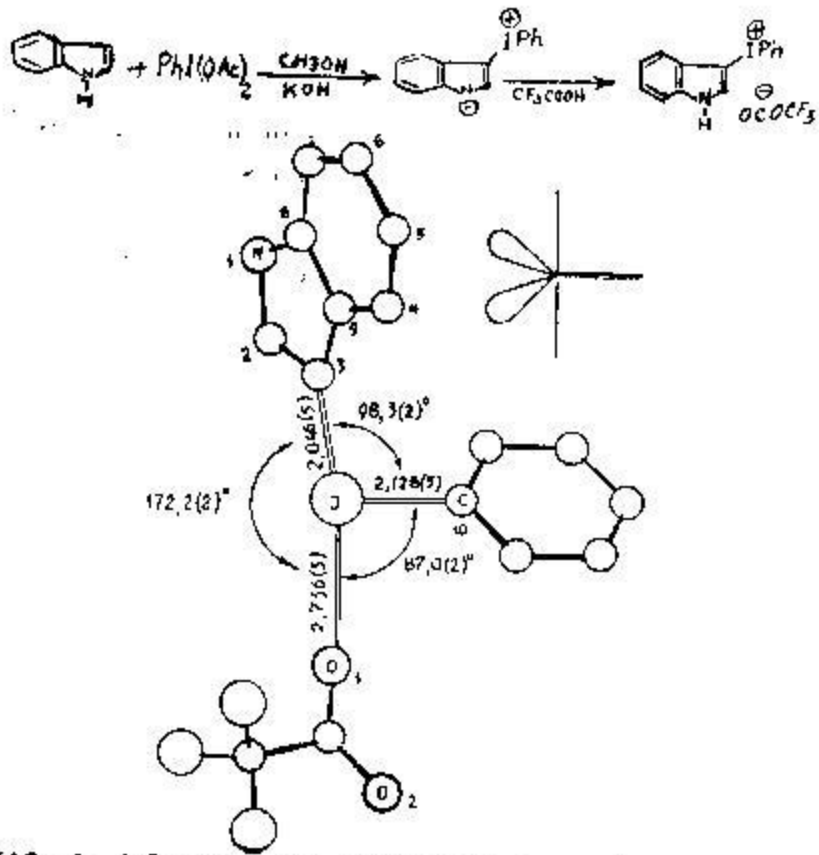

FIG. 1. MOLECULAR STRUCTURE OF (INDOLYL-3) PHENYL TRIFLUOROACETATE

It is of interest to note that the bond I-O1 (2.74 Å) is longer than that of a normal covalent bond (2.16 Å in phenyl iodosodiacetate) but shorter than the

ionic bond (sum of vander waals radii 3.45 Å), indicating that the bond dissociation energy would be considerably less the normal single bond energy. Bond lengths and bond angles in both cyclic rings have standard meaning for benzol rings 1.39 Å and 120°, for pyrrol ring $C^2-C^3=1.38$ Å, $NC^2C^3=C^2C^3C^9=108°$.

CONCLUSION

These findings have led to the precise structure, for the first time, of an iodonium salt having indolyl group as a ligand.

REFERENCES

Chughtai, F.A., Ermolenko, M.S. and Budylin, V.A. 1981. Reaction of betain (Indolyl-3) phenyl iodonium with electrophilic reagents. Khimia Getro. Soed. SSSR 11: 1503-1505 (Russ).

Khotsyanova, T.L. 1975. Crystal structure of diphenyl iodonium iodide. Dokl. Akad. Nauk SSSR, 232 : 147 (Russ).

Khotsyanova, T.L. 1976. Crystal structure of diphenyl iodonium bromide. Koordinatsionaya Khimia 2: 1567-1569 (Russ).

Khotsyanova, T.L. 1957. Crystal structure of diphehyl iodonium halides. Kristallografia 2 : 51-58. (Russ).

Pausacker, K H. 1953. The oxidation of glycols by aryl iodosoacetates. J. Chem. Soc. I : 107-109.

Struchkov, Yu. T. and T.L. Khotsyanova. 1960. Crystal structure of diphenyl iodonium fluoroborate. Izv. Akad. Nauk SSSR, 821 (1960) (Chem. Abst., 55 : 11028, 1962).

Yamada, Y. and Okawara, M. 1972. Steric effect in the nucleophilic attack of bromide anion on diaryl and aryl-2-thienyliodonium ions. Bull. Chem. Soc. Jap. 45 : 1860-1863.