Journal of Fluorine Chemistry, 5 (1975) 467 – 474

Received: December 10, 1974

SYNTHESIS AND CRYSTAL STRUCTURE OF p-BROMOPHENYLDIPHENYLCARBINYL DIFLUORAMINE

Jefferson R. Surles, Carl L. Bumgardner, and Jon Bordner

Department of Chemistry, North Carolina State University,
Raleigh, North Carolina 27607

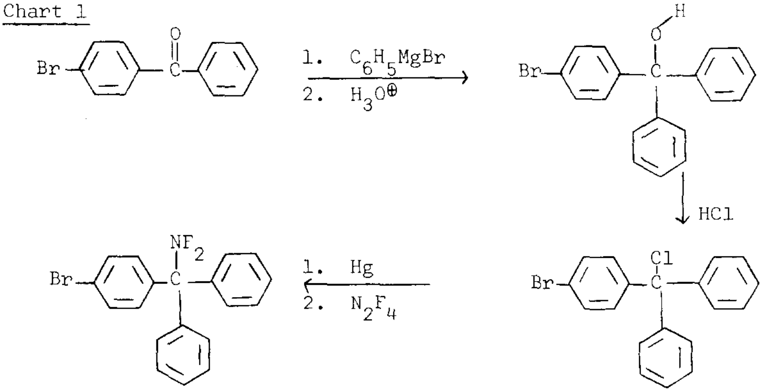
INTRODUCTION

Current interest in organic NF_2 compounds--, particularly those having biological activity--, prompted us to synthesize a crystalline difluoramine derivative suitable for x-ray analysis. Using as a guide the method described by Graham and Parker[1] for the preparation of trityldifluoramine from trityl alcohol, we undertook the conversion of p-bromophenyldiphenylcarbinol to p-bromophenyldiphenylcarbinyl difluoramine whose heavy atom would facilitate determination of structural detail. This report deals with the successful synthesis and x-ray analysis of p-bromophenyldiphenylcarbinyl difluoramine which provides, for the first time, information concerning the FNF bond angle and NF bond length in an NF_2 group bound to a saturated carbon.

SYNTHESIS

The general scheme is outlined in Chart 1.

Chart 1



Addition of phenyl Grignard reagent to p-bromobenzophenone gave p-bromophenyldiphenylcarbinol which was converted to the chloride by the action of concentrated HCl. Treatment of a nitrobenzene solution of p-bromophenyldiphenylcarbinyl chloride with mercury in an atmosphere of N_2F_4 produced the desired difluoramine in 6.23% overall yield. Analytical and spectroscopic results (see Experimental) are consistent with the proposed structure.

X-RAY ANALYSIS

The structure of 1 was established by a single crystal x-ray analysis. Crystals were grown by a slow evaporation technique and cut to an appropriate size (Table 1). The crystal was surveyed and 1-Å intensity data set (maximum sin $\theta/\lambda = 0.5$) collected on a Syntex $P\bar{1}$ diffractometer at room temperature. The

Table 1. Crystal and Data Collection Parameters

Crystallization medium	Methanol
Crystal size	0.2x0.2x0.2 mm
Space group	$P2_1/n$

Cell dimensions	a=11.091(3);
	b=9.322(2);
	c=15.720(4)Å;
	β=95.19(2)°

Density observed	1.48 g/cm^3
Density calculated (Z=4)	1.52 g/cm^3
Scan mode	$\theta/2\theta$
Scan rate	4°/min in 2θ
Background count time	1/2 peak scan time (at both ends of
No. of reflections	1666
Non-zero reflections	1516

diffractometer was equipped with a graphite monochromator mounted in a perpendicular mode and copper radiation (λ = 1.5418Å). Crystal and data collection parameters are presented in Table 1.

All crystallographic calculations were facilitated by the use of the CRYM crystallographic computer program system (Duchamp, 1964)[2]. The trial structure was derived by conventional Patterson and Fourier techniques. This trial structure refined smoothly to a final R index of 0.050. A final difference Fourier revealed no missing or misplaced atoms. The final cycles of full-matrix least-squares contained the coordinates, scale factor, and anisotropic temperature factors for non-hydrogen atoms in one matrix. The hydrogen parameters were not refined.

The structure obtained in the analysis was stereographically plotted using the ORTEP computer program of C. K. Johnson[3] (Figure 1). The bond distances and angles with their standard deviations are summarized in Table 2. Heavy atom parameters, their standard deviations, and temperature factors are given in Table 3. The calculated hydrogen parameters and the isotropic temperature factor are in Table 4. The structure factor table is available on request.

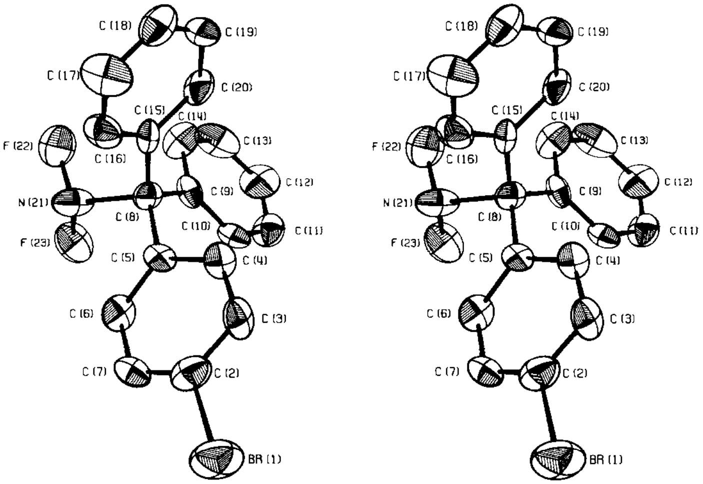


Figure 1. Stereoplot of 1

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) WITH THEIR STANDARD DEVIATIONS

Bond	Distance	Bond	Distance
1-2	1.900(4)	9-14	1.395(7)
2-3	1.379(8)	10-11	1.404(7)
2-7	1.368(8)	11-12	1.372(8)
3-4	1.386(7)	12-13	1.370(8)
4-5	1.389(7)	13-14	1.376(7)
5-6	1.393(7)	15-16	1.386(7)
5-8	1.535(6)	15-20	1.381(7)
6-7	1.399(7)	16-17	1.382(9)
8-9	1.536(6)	17-18	1.374(9)
8-15	1.525(7)	18-19	1.372(8)
8-21	1.528(6)	19-20	1.397(8)
9-10	1.388(7)	21-22	1.406(5)
		21-23	1.417(5)

Atoms	Angle	Atoms	Angle	Atoms	Angle
3-2-1	119.2(4)	15-8-5	107.5(4)	16-15-8	119.1(4)
7-2-1	119.2(4)	15-8-9	115.0(4)	20-15-8	122.2(4)
7-2-3	121.6(4)	21-8-9	111.2(4)	20-15-16	118.5(5)
4-3-2	118.4(5)	21-8-15	104.7(4)	17-16-15	121.0(5)
5-4-3	122.0(5)	10-9-8	121.5(4)	18-17-16	120.2(5)
6-5-4	118.1(4)	14-9-8	120.6(4)	19-18-17	119.6(6)
8-5-4	117.9(4)	14-9-10	117.9(4)	20-19-18	120.4(5)
8-5-6	123.9(4)	11-10-9	121.4(4)	19-20-15	120.3(5)
7-6-5	120.3(5)	12-11-10	119.3(5)	22-21-8	107.2(3)
6-7-2	119.5(5)	13-12-11	119.6(5)	23-21-8	105.9(3)
9-8-5	113.3(4)	14-13-12	121.7(5)	23-21-22	100.1(3)
21-8-5	104.1(4)	13-14-9	120.1(5)		

DISCUSSION

Our data allow some interesting comparisons to be made. The N-F bond distance was found to be 1.42-2Å, which is longer than that reported for the bond in CH_2F_2 (1.36Å)[4]. This is understandable since unshared electron repu

TABLE 3

HEAVY ATOM PARAMETERS (X10^4) AND THEIR STANDARD DEVIATIONS IN PARENTHESIS

THE TEMPERATURE FACTOR IS IN THE FORM:

$$\exp[-(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + U_{12}hk + U_{13}hl + U_{23}kl)]$$

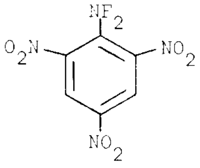
Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	7282(1)	3703(1)	4332(0)	96(1)	100(1)	47(0)	1(1)	24(0)	7(0)
C (2)	6811(4)	3509(6)	5459(3)	47(4)	69(4)	30(3)	-12(3)	7(3)	4(3)
C (3)	7126(4)	2284(6)	5917(3)	51(4)	54(4)	43(3)	0(3)	6(3)	-4(3)
C (4)	6786(4)	2167(6)	6741(3)	53(4)	44(4)	44(3)	4(3)	2(3)	4(3)
C (5)	6163(4)	3254(5)	7118(3)	32(3)	38(4)	39(3)	-3(3)	-2(2)	-1(3)
C (6)	5867(4)	4483(6)	6640(3)	46(4)	44(4)	46(3)	5(3)	-1(3)	-1(3)
C (7)	6207(5)	4613(6)	5807(3)	54(4)	52(4)	45(3)	3(3)	-1(3)	8(3)
C (8)	5784(4)	2994(5)	8020(3)	36(3)	42(4)	38(3)	4(3)	0(2)	-2(3)
C (9)	6838(4)	3121(5)	8720(3)	42(4)	39(4)	44(3)	0(3)	0(3)	-4(3)
C(10)	8007(4)	3422(5)	8524(3)	46(3)	36(3)	47(3)	-1(3)	-2(3)	0(3)
C(11)	8967(4)	3553(6)	9166(4)	46(4)	47(4)	65(4)	-5(3)	-7(3)	0(3)
C(12)	8744(5)	3376(6)	10004(3)	61(4)	68(5)	54(4)	-8(4)	-22(3)	-5(3)
C(13)	7595(5)	3056(7)	10200(3)	79(5)	97(5)	31(3)	-6(4)	-6(3)	-1(3)
C(14)	6648(5)	2919(7)	9577(3)	50(4)	93(5)	38(3)	-8(4)	0(3)	-6(3)
C(15)	5099(4)	1579(6)	8006(3)	33(3)	52(4)	36(3)	-4(3)	3(2)	-5(3)
C(16)	4050(4)	1424(6)	7463(3)	50(4)	67(4)	42(3)	-10(3)	-2(3)	5(3)
C(17)	3460(5)	119(8)	7372(3)	57(4)	99(6)	47(4)	-29(4)	-3(3)	-6(4)
C(18)	3916(5)	-1060(7)	7816(4)	61(4)	72(5)	69(4)	-24(4)	18(3)	-15(4)
C(19)	4945(5)	-928(6)	8364(4)	63(4)	53(4)	86(4)	0(4)	17(4)	10(4)
C(20)	5540(4)	392(6)	8463(3)	40(3)	52(4)	62(4)	-1(3)	-1(3)	3(3)
N(21)	4821(4)	4136(5)	8126(3)	59(3)	57(3)	52(3)	1(3)	14(2)	-10(2)
F(22)	4316(3)	3844(4)	8897(2)	76(2)	84(3)	70(2)	10(2)	28(2)	-5(2)
F(23)	5463(3)	5414(3)	8353(2)	85(2)	47(2)	70(2)	6(2)	3(2)	-13(2)

TABLE 4

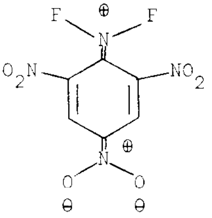
CALCULATED HYDROGEN PARAMETERS ($\times 10^4$) ISOTROPIC TEMPERATURE FACTOR EQUALS 4.37

Atom	A+	X	Y	Z
H(24)	C(3)	7634	1434	5646
H(25)	C(4)	7028	1208	7104
H(26)	C(6)	5382	5347	6915
H(27)	C(7)	5983	5584	5444
H(28)	C(10)	8172	3560	7857
H(29)	C(11)	9871	3785	9007
H(30)	C(12)	9468	3485	10500
H(31)	C(13)	7430	2898	10859
H(32)	C(14)	5752	2663	9742
H(33)	C(16)	3691	2349	7104
H(34)	C(17)	2631	20	6960
H(35)	C(18)	3459	-2076	7718
H(36)	C(19)	5294	-1843	8739
H(37)	C(20)	6353	490	8908

is greater in the case of the NF compound. In 2,4,6-trinitro-N,N-difluoraniline where the NF_2 group is attached to aromatic carbon, the N-F distance was reported to be 1.397Å[5]. One is tempted to attribute the difference in aliphatic and aromatic NF bond distances to resonance interactions exemplified by structure I.



2

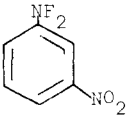


I

Consistent with this idea is the finding that the C-N bond length in our compound (1.528Å) is longer than that reported by Batail, et al. (1.461Å) for 2. Moreover the FNF bond angle in compound 1 (100.1°) is significantly less than the FNF angle in compound 2 (102.28°).

Comparison of the CNF bond angles, however, does not reveal any significant differences between 1 (106-107°) and 2 (105.07°). If structure I and other similar resonance forms were contributing to 2 the CNF bond angle in the aromatic case would be expected to be greater than that in 1, where the NF_2 is attached to aliphatic carbon.

Obviously additional compounds need to be studied before concrete conclusions can be drawn regarding the relative importance of resonance structures exemplified by I. Determination of the pertinent bond angles and lengths in m-nitro N,N-difluoraniline (3), where conjugation of the amine and nitro groups is not possible, would be particularly informative.


3

EXPERIMENTAL

Preparation of p-bromophenyldiphenylcarbinyl chloride

To 5.67 g of magnesium metal turnings was added 100 ml of dry ethyl ether. Previously dried bromobenzene (36.11 g) was added to the refluxing ether over a 30 min. period. The Grignard solution was stirred and refluxed for another 30 min., then 60 g of 4-bromobenzophenone (Aldrich) in 200 ml dry benzene was added dropwise. The resulting mixture was heated for 30 min., then cooled and poured onto 1000 g of ice containing 30 ml of H_2SO_4. The slush was stirred and another 100 ml ether was added. The non-aqueous portion was separated, washed with 100 ml of water, 5% sodium bicarbonate solution, 100 ml of water, and dried over $MgSO_4$. The mixture was filtered and the ether-benzene was removed under vacuum. No crystals could be obtained and IR analysis showed some unchanged ketone present. The viscous brown mixture was treated with 75 ml of conc. HCl and the non-aqueous portion was taken up in ether, washed with 5% $NaHCO_3$, water and dried over $MgSO_4$. The drying agent was removed by filtration and the solvent was removed under vacuum leaving a viscous yellow liquid. Overnight crystals formed which were removed by filtration and washed with ligroin. IR analysis showed absences of absorptions in the 3400-3100 cm^{-1} and 1750-1600 cm^{-1} regions but the melting point (101-2°) disagreed with a previously reported value (114°)[6].

Preparation of p-bromophenyldiphenylcarbinyl difluoramine

Satisfactory results were obtained using the method described by Graham a Parker[1] for the preparation of trityldifluoramine. Colorless crystals, mp 84° were obrained in 60% yield (based on chloride) and the mass spectrum was consi with the desired compound. The ^{19}F NMR spectrum consisted of a singlet at -31. downfield from CFCl$_3$. Resonance for the fluorine in trityldifluoramine was ob at -32.4 ϕ.[7]

Anal. Calcd. for $C_{19}H_{14}BrNF_2$: C, 60.96; H, 3.74; Br, 21.39; N, 3.74; F, 10.1 Found: C, 61.00; H, 3.66; Br, 21.22; N, 3.69; F, 10.07.

REFERENCES

1. W. H. Graham and C. O. Parker, *J. Org. Chem.,* **28**, (1963), 850.
2. D. J. Duchamp, (1964), Amer. Cryst. Assoc. Meeting, Bozeman, Montana, paper B-14, p. 29.
3. C. K. Johnson, ORTEP, ORNL-3794, Oak Ridge National Laboratories, Oak Ridge Tennessee.
4. Hencher and Bauer, *J. Am. Chem. Soc.,* **89**, (1967), 5527.
5. P. Batail, D. Grandjean, F. Dudragne, and C. Michaud, (1974), 5th European Symposium on Fluorine Chemistry, Aviemore, Scotland, paper O 21, p. 139.
6. C. S. Marvel, F. C. Dietz, and C. M. Himel, *J. Org. Chem.,* **7**, (1972), 392.
7. W. H. Graham, and J. P. Freeman, *J. Amer. Chem. Soc.,* **89**, (1967), 716.