[CONTRIBUTION FROM THE DYSON PERRINS LABORATORY, OXFORD, ENGLAND, AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Use of Fluoro Compounds in the Determination of Valency Angles by Electric Dipole Moment Measurements

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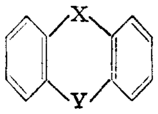
Our initial aim in this investigation was to determine bond angles from electric dipole substitution, using methods previously developed[1,2,3,4] but using fluorine as the substituent atom. Evaluations of the interaction moments between halogens and the NH_2- or CH_3O- grouping indicated that these are least with fluorine,[5] and therefore that this cause of error in bond angle determinations should be least if fluorine is used. Our results caused us to investigate more thoroughly the magnitudes of such interaction moments in fluorine compounds, and to compare them with those for other halogens.

We applied information so obtained about bond angles in the discussion of the configuration of molecules of the type I, when X and Y are divalent atoms or groups, *e. g.*, O, S, Se, NH, and we augmented the dipole moment data for such compounds by measuring phenoxthine and phenthiazine.



I

Experimental

Preparation and Purification of Materials.—Benzene (British Drug Houses "AnalaR") was purified by freezing three times, boiling under reflux over phosphorus pentoxide, and finally distilling in a dry air stream. It was stored under dry air until used.[2] Diphenylamine (B. D. H.) was recrystallized four times from dry petroleum ether (b. p. 40–60°), m. p. 53°. Di-*p*-tolylamine (B. D. H.) was recrystallized twice from dry petroleum ether, m. p. 79°.

The following compounds were prepared by methods previously described: fluorobenzene,[6] *p*-fluoroaniline,[7] *p*-fluoroanisole,[8] *p*-fluorobenzaldehyde,[9] *p*-fluorobromobenzene,[10] *p*-fluoronitrobenzene,[11] *p*-fluorobenzophenone,[13] *p*-fluorophenol,[12] *p*-fluorotoluene,[11] *p,p'*-difluorobenzophenone,[13] phenyl-*p*-tolylamine,[14] phenyl-*p*-tolylnitrosamine, m. p. 82°,[15] di-*p*-tolylnitrosamine, m. p. 100–101°,[15] phenoxthine,[16] phenthiazine,[17] and triphenylamine.[18]

The compounds described below are, with one exception, new compounds, prepared specifically for the presently described dipole moment investigation.

***p*-Fluorodimethylaniline.**—This compound had previously been prepared by Schiemann and Pillarsky[19] from *p*-aminodimethylaniline, but a better yield was obtained by methylation of *p*-fluoroaniline. A mixture of 20 g. of dimethyl sulfate and 17 g. of *p*-fluoroaniline was sealed in a pressure tube and heated at 200° for one hour. The oily product was treated with aqueous sodium hydroxide and the resultant mixture was extracted with ether. After drying the ethereal solution, the ether was removed and the residue was distilled *in vacuo*, b. p. 86–87° (18 mm.), 79.5° (16 mm.); yield, 15 g. (71.5%).

***p*-Fluorodiphenyl Ether.**—A method similar to that used for *p*-tolyl- and di-*o*-tolyl ether by Reilly, Drumm and Barrett[20] was employed. A mixture of 12 g. of potassium *p*-fluorophenoxide, 12 g. of bromobenzene, and 0.5 g. of copper-bronze was heated at 200° for four hours under an air condenser. The product was subjected to steam distillation and the distillate was extracted with ether. The ethereal solution was dried and the ether was removed. The liquid residue was fractionated at atmospheric pressure. The portion boiling above 200° was retained and twice fractionated. Seven grams (47%) of colorless liquid, b. p. 247–249° (760 mm.), was finally collected.

Anal. Calcd. for $C_{12}H_9FO$: C, 76.59; H, 4.79. Found: C, 76.25; H, 4.82.

***p,p'*-Difluorodiphenyl Ether.**—Twelve grams of potassium *p*-fluorophenoxide, 15 g. of *p*-fluorobromobenzene, and 0.5 g. of copper-bronze were mixed and the mixture was heated under reflux for six hours at 200°. The product was isolated by the same method as employed for *p*-fluorodiphenyl ether. The colorless liquid boiled at 239–240° (743 mm.); yield, 9.0 g. (56%).

Anal. Calcd. for $C_{12}H_8F_2O$: C, 69.88; H, 4.01. Found: C, 70.08; H, 3.94.

***p*-Fluorodiphenyl Sulfide.**—A method similar to that used by Mauthner[21] for analogous sulfides was employed. Fourteen grams of potassium thiophenoxide, 29 g. of *p*-fluoroiodobenzene, and 0.5 g. of copper-bronze were heated together under reflux at 235–240° for four hours. The reaction product was treated with warm ethanol and acidified with dilute sulfuric acid. After the addition of zinc dust, the mixture was steam-distilled. The distillate was extracted with ether, the ethereal solution was dried and the ether was removed. The colorless product was distilled once with fractionation at atmospheric pressure, then twice at reduced pressure, b. p. 147–148° (15 mm.), 141–142° (11 mm.); yield, 18 g. (66%).

Anal. Calcd. for $C_{12}H_9FS$: C, 70.58; H, 4.44. Found: C, 70.25; H, 4.35.

***p,p'*-Difluorodiphenyl Sulfoxide.**—This compound was prepared successfully by the method which Colby and McLoughlin[22] used for diphenyl sulfoxide. Sixty grams of fluorobenzene and 16 g. of thionyl chloride were mixed in

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[1] Hampson and Sutton, *Proc. Roy. Soc.* (*London*), **140A**, 562 (1933).

[2] Hampson, Farmer and Sutton, *ibid.*, **143A**, 147 (1933).

[3] Sutton and Hampson, *Trans. Faraday Soc.*, **31**, 945 (1935).

[4] Coop and Sutton, *J. Chem. Soc.*, 1869 (1938).

[5] Marsden and Sutton, *ibid.*, 599 (1936).

[6] "Organic Syntheses," **13**, 46 (1933).

[7] Schiemann and Pillarsky, *Ber.*, **62**, 3035 (1929).

[8] Bergmann and Tschudnowsky, *Z. physik. Chem.*, **17B**, 107 (1932).

[9] Schiemann, *ibid.*, **156A**, 397 (1931).

[10] Schiemann and Pillarsky, *Ber.*, **64**, 1340 (1931).

[11] Balz and Schiemann, *ibid.*, **60**, 1186 (1927).

[12] Bennett, Brooks and Glasstone, *J. Chem. Soc.*, 1821 (1935).

[13] Dunlop and Gardner, THIS JOURNAL, **55**, 1665 (1933).

[14] Chapman, *J. Chem. Soc.*, 569 (1929).

[15] Lachman, *Ber.*, **33**, 1022 (1900).

[16] "Organic Syntheses," **18**, 64 (1938).

[17] Kehrmann and Dardel, *Ber.*, **55**, 2346 (1922).

[18] "Organic Syntheses," **8**, 116 (1928).

[19] Schiemann and Pillarsky, *Ber.*, **66**, 727 (1933).

[20] Reilly, Drumm and Barrett, *J. Chem. Soc.*, 67 (1927).

[21] Mauthner, *Ber.*, **39**, 3593 (1906).

[22] Colby and McLoughlin, *ibid.*, **20**, 195 (1887).

an ice-cooled flask to which a reflux condenser was attached. Anhydrous aluminum chloride was added in small portions; hydrogen chloride ceased to be evolved after 40 g. had been added. The mixture was heated on a water-bath for thirty minutes, after which it was cooled and poured into ice-water. The thick oil which separated on the surface was washed with water and was then heated to remove excess fluorobenzene. A yellow, wax-like solid remained which was recrystallized three times from petroleum ether (b. p. 40-60°). A yield of 23 g. (72%) of colorless crystals, m. p. 50.5°, was obtained.

Anal. Calcd. for $C_{12}H_8F_2OS$: C, 60.47; H, 3.39. Found: C, 60.26; H, 3.55.

***p,p'*-Difluorodiphenyl Sulfide.**—This compound was prepared by a method analogous to that of Gazdar and Smiles[23] for di-*p*-cresol sulfide. *p,p'*-Difluorodiphenyl sulfoxide (17 g.) was boiled for four hours under reflux with 6 g. of powdered zinc in glacial acetic acid. When the filtered solution was diluted with water, the sulfide separated as a colorless oil, which was twice fractionally distilled *in vacuo*, b. p. 136-137° (9 mm.); yield, 15 g. (90%).

Anal. Calcd. for $C_{12}H_8F_2S$: C, 64.83; H, 3.63. Found: C, 64.71; H, 3.51.

***p,p'*-Difluorodiphenyl Sulfone.**—*p,p'*-Difluorodiphenyl sulfide (5 g.) was dissolved in a ten-fold quantity of glacial acetic acid and oxidized with 3 g. of potassium permanganate. After dilution of the reaction mixture with water, the precipitate was twice recrystallized from ethanol as colorless needles, m. p. 98-98.5°; yield, 4 g. (80%).

Anal. Calcd. for $C_{12}H_8F_2O_2S$: C, 56.67; H, 3.17. Found: C, 56.34; H, 3.18.

***p*-Fluorodiphenyl Sulfone.**—This compound was prepared in the same manner, using 8.5 g. of *p*-fluorodiphenyl sulfide, 80 g. of glacial acetic acid, and 6 g. of potassium permanganate. After dilution of the reaction mixture with water, the precipitate was twice recrystallized from ethanol as colorless needles, m. p. 109.5-110°; yield, 6 g. (70%).

Anal. Calcd. for $C_{12}H_9FO_2S$: C, 60.98; H, 3.84. Found: C, 60.97; H, 3.76.

***p*-Fluorodiphenylamine.**—This compound, b. p. 164-166° (17 mm.), m. p. 34°, was made from *p*-fluoroacetanilide and bromobenzene essentially by the method of Goldberg,[24] which is general for the preparation of diarylamines.

Anal. Calcd. for $C_{12}H_{10}FN$: C, 76.99; H, 5.38. Found: C, 76.89; H, 5.32.

***p,p'*-Difluorodiphenylamine.**—This compound, b. p. 165-166.5° (17 mm.), m. p. 37.5°, was likewise prepared from *p*-fluoroacetanilide and *p*-fluorobromobenzene by the general method of Goldberg.[24]

Anal. Calcd. for $C_{12}H_9F_2N$: C, 70.24; H, 4.40. Found: C, 70.37; H, 4.46.

***p*-Fluorotriphenylamine.**—A method similar to that for triphenylamine[18] was employed. A mixture of 8 g. of diphenylamine, 13 g. of *p*-fluoroiodobenzene, 8 g. of potassium carbonate, and 2 g. of copper-bronze in 50 ml. of nitrobenzene was boiled under reflux for ten hours. The nitrobenzene was removed by steam distillation and the residue was extracted with benzene. The benzene extract was dried by partial distillation of benzene, saturated with dry hydrogen chloride gas in the cold, and allowed to stand for three hours. The precipitated diphenylamine hydrochloride was removed by filtration and the benzene by distillation. The residue was distilled under reduced pressure, b. p. 187-189° (8 mm.), when the distillate solidified. Three recrystallizations from ethanol, followed by centrifuging and drying, gave 7 g. (60%) of colorless needles, m. p. 98-98.5°.

Anal. Calcd. for $C_{18}H_{14}FN$: C, 82.09; H, 5.32. Found: C, 82.22; H, 5.31.

Physical Measurements.—Electric dipole moments were determined from measurements of the dielectric constant, refractive index and density of benzene solutions of varying concentration at the same temperature. Dielectric constants were determined by a heterodyne beat method using an apparatus and a technique essentially the same as described before.[2,25] The solution condenser was similar to that described by Jenkins and Sutton.[26]

Densities were determined with a 10-ml. Sprengel-Ostwald pyknometer.

Refractive indices were measured relative to the solvent with a Pulfrich refractometer fitted with a divided cell; the mercury green line (5461 Å.) was used for illumination. For three of the compounds (fluorobenzene, *p*-fluorodiphenyl sulfide, and *p*-fluorotriphenylamine) it was not possible to obtain the molecular refractivities experimentally, due to temporary instrumental disorder, but they were calculated from the most acceptable values for the refractivities of the constituent atoms.

The dielectric constant of pure dry benzene was taken to be 2.2727 at 25°, that of dry air 1.0000. The square of the refractive index of pure dry benzene at 25° was taken to be 2.25714.

Atom polarizations, for the moments recorded in Table I, were allowed by adding 5% to the electron polarization.

Results

All measurements are in benzene solution at 25°. Moments are expressed in Debye units (1 D = 10^{-18} e. s. u.).

TABLE I

DIPOLE MOMENTS IN BENZENE AT 25°

Compound	$_{A}P = 0$	$_{A}P = 5\%_{E}P$
Fluorobenzene	1.45	1.53
p-Fluoroaniline	2.48	2.46
p-Fluoroanisole	2.06	2.04
p-Fluorobenzaldehyde	1.98	1.96
p-Fluorobromobenzene	0.22	0.0
p-Fluorodimethylaniline	2.69	2.67
p-Fluoronitrobenzene	2.64	2.62
p-Fluorophenol	2.10	2.08
p-Fluorotoluene	1.71	1.68
Diphenyl ether	1.16[2]	1.11
p-Fluorodiphenyl ether	1.39	1.35
p,p'-Difluorodiphenyl ether	0.62	0.51
Diphenyl sulfide	1.50[2]	1.45
p-Fluorodiphenyl sulfide	1.42	1.37
p,p'-Difluorodiphenyl sulfide	0.61	0.48
Diphenyl sulfoxide	3.99[2]	3.97
p,p'-Difluorodiphenyl sulfoxide	2.67	2.64
Di-*p*-tolyl sulfoxide	4.40[2]	4.38
Diphenyl sulfone	5.05[32]	5.04
p-Fluorodiphenyl sulfone	4.28	4.26
p,p'-Difluorodiphenyl sulfone	3.31	3.28
Benzophenone	2.96[33]	2.93
p-Fluorobenzophenone	2.67	2.63
p,p'-Difluorobenzophenone	1.78	1.74
Diphenylamine	1.04	0.99
p-Fluorodiphenylamine	1.89	1.86
p,p'-Difluorodiphenylamine	2.12	2.09

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(23) Gazdar and Smiles, *J. Chem. Soc.*, **97**, 2248 (1910).

(24) Godberg, *Ber.*, **40**, 4541 (1907).

(25) Sutton, *Proc. Roy. Soc. (London)*, **133A**, 668 (1931).

(26) Jenkins and Sutton, *J. Chem. Soc.*, 609 (1935).

(27) Calculated from the atomic refractivities.

(28) Audsley and Goss (*J. Chem. Soc.*, 497 (1942)) reported 1.44; Bergmann, Engel and Sandor (*Z. physik. Chem.*, **10B**, 106 (1930)). 1.45.

TABLE I (*Continued*)

Compound	$_AP = 0$	$_AP = 5\%{}_EP$
Phenyl-*p*-tolylamine	1.12	1.01
Di-*p*-tolylamine	1.05	0.93
Diphenylnitrosamine	3.39[34]	3.35
Phenyl-*p*-tolylnitrosamine	3.59	3.54
Di-*p*-tolylnitrosamine	3.83	3.79
Triphenylamine	0.71[35]	0.55
p-Fluorotriphenylamine	1.47	1.40
Phenoxthine	1.00	0.92
Phenthiazine	2.16	2.13

Fluorobenzene

f_2	d^{25}_4	ϵ	n^2	P_2	$_EP_2$
0.00541	0.8742	2.2883	....	70.76	
.01161	.8751	2.3064	....	70.47	
.02099	.8765	2.3324	....	69.50	26.2[27]
.03142	.8880	2.3618	....	69.22	

$_\infty P_2 = 71.0$; $_EP_2 = 26.2$; $_OP_2 = 44.8$ cc.; $\mu = 1.46 \pm 0.02$ D[28]

p-Fluoroaniline

0.00631	0.8756	2.3285	2.2581	155.5	29.4
.01459	.8784	2.4025	2.2591	154.4	29.3
.02232	.8810	2.4728	2.2605	153.4	29.5
.03456	.8853	2.5854	2.2624	151.3	29.4

$_\infty P_2 = 156.7$; $_EP_2 = 29.4$; $_OP_2 = 127.3$ cc.; $\mu = 2.48 \pm 0.01$ D[29]

p-Fluoroanisole

0.00439	0.8746	2.2991	2.2575	122.1	35.4
.00911	.8759	2.3276	2.2577	122.3	35.3
.01411	.8773	2.3577	2.2578	121.7	35.0
.02225	.8795	2.4067	2.2583	120.9	35.1

$_\infty P_2 = 123.2$; $_EP_2 = 35.2$; $_OP_2 = 88.0$ cc.; $\mu = 2.06 \pm 0.01$ D[8]

p-Fluorobenzaldehyde (in atmosphere of nitrogen)

0.00680	0.8759	2.3109	2.2576	113.5	32.4
.00844	.8765	2.3194	2.2577	112.2	32.5
.01385	.8784	2.3495	2.2579	112.0	32.4
.01782	.8797	2.3717	2.2580	111.8	32.3

$_\infty P_2 = 113.7$; $_EP_2 = 32.4$; $_OP_2 = 81.3$ cc.; $\mu = 1.98 \pm 0.01$D

p-Fluorobromobenzene

0.00753	0.8799	2.2742	2.2580	35.37	33.9
.01528	.8868	2.2757	....	35.21	..
.02771	.8973	2.2778	2.2598	35.70	34.1

$_\infty P_2 = 35.0$; $_EP_2 = 34.0$; $_OP_2 = 1.0$ cc.; $\mu = 0$–0.22 D

p-Fluorodimethylaniline

0.00473	0.8749	2.3217	2.2579	188.0	39.3
.01073	.8769	2.3846	2.2587	187.0	38.9
.02149	.8803	2.4993	2.2598	185.9	39.0
.03067	.8834	2.5958	2.2607	183.0	38.7

$_\infty P_2 = 188.7$; $_EP_2 = 39.0$; $_OP_2 = 149.7$ cc.; $\mu = 2.69 \pm 0.01$D

p-Fluoronitrobenzene

f_2	d^{25}_4	ϵ	n^2	P_2	$_EP_2$
0.00484	0.8759	2.3206	....	175.0	..
.00956	.8787	2.3671	2.2581	172.5	31.6
.01912	.8837	2.4589	2.2588	168.8	32.3
.02546	.8876	2.5226	2.2595	167.6	31.9

$_\infty P_2 = 176.3$; $_EP_2 = 31.9$; $_OP_2 = 144.4$ cc.; $\mu = 2.64 \pm 0.01$D[30]

p-Fluorophenol

0.00621	0.8757	2.3117	2.2577	119.2	29.1
.01255	.8781	2.3517	2.2580	118.1	28.2
.02242	.8811	2.4138	2.2584	117.6	28.6
.03611	.8860	2.5001	....	115.6	..

$_\infty P_2 = 119.9$; $_EP_2 = 28.6$; $_OP_2 = 91.3$ cc.; $\mu = 2.10 \pm 0.01$D

p-Fluorotoluene

0.00684	0.8742	2.3016	2.2580	95.02	34.9
.01346	.8751	2.3295	2.2588	94.68	35.0
.01817	.8757	2.3496	2.2595	94.69	35.0
.03312	.8777	2.4128	2.2616	94.04	35.1

$_\infty P_2 = 95.3$; $_EP_2 = 35.0$; $_OP_2 = 60.3$ cc.; $\mu = 1.71 \pm 0.01$D

p-Fluorodiphenyl Ether

0.00470	0.8758	2.2870	2.2587	92.36	52.5
.00725	.8771	2.2946	....	92.59	..
.01571	.8815	2.3197	2.2621	92.13	52.4
.03146	.8896	2.3657	2.2676	91.50	52.6

$_\infty P_2 = 92.8$; $_EP_2 = 52.5$; $_OP_2 = 40.3$ cc.; $\mu = 1.39 \pm 0.01$D

p,p'-Difluorodiphenyl Ether

0.00430	0.8762	2.2758	....	60.83	..
.00790	.8786	2.2782	2.2587	60.49	52.8
.01334	.8822	2.2824	2.2599	60.55	52.5
.02016	.8864	2.2758	2.2614	60.73	53.0

$_\infty P_2 = 60.7$; $_EP_2 = 52.7$; $_OP_2 = 8.0$ cc.; $\mu = 0.62 \pm 0.02$D

p-Fluorodiphenyl Sulfide

0.00401	0.8758	2.2867	....	102.6	
.01014	.8798	2.3087	....	102.6	61.1[27]
.01848	.8848	2.3364	....	101.6	
.02629	.8895	2.3624	....	101.1	

$_\infty P_2 = 102.9$; $_EP_2 = 61.1$; $_OP_2 = 41.8$ cc.; $\mu = 1.42 \pm 0.01$D

p,p'-Difluorodiphenyl Sulfide

0.00372	0.8762	2.2769	2.2593	68.88	60.5
.00686	.8785	2.2801	....	68.86	..
.01083	.8815	2.2844	2.2640	68.56	59.6
.02586	.8928	2.3012	2.2704	68.75	61.7

$_\infty P_2 = 68.7$; $_EP_2 = 60.9$; $_OP_2 = 7.8$ cc.; $\mu = 0.61 \pm 0.03$D

p,p'-Difluorodiphenyl Sulfoxide

0.00480	0.8779	2.3238	....	207.6	..
.00961	.8824	2.3742	....	205.2	..

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[29] Bergmann and Tschudnowsky (*Z. physik. Chem.*, **17B**, 100 (1932)) reported 2.75.

[30] Bergmann, Engel and Sandor (*Z. physik. Chem.*, **10B**, 397 (1930)) reported 2.63.

TABLE I (*Continued*)

f_2	d^{25}_4	ϵ	n^2	P_2	$_EP_2$
.01658	.8887	2.4474	2.2662	203.6	60.3
.02252	.8943	2.5092	2.2696	201.7	60.3

$_\infty P_2$ = 209.0; $_EP_2$ = 60.3; $_OP_2$ = 148.7 cc.; μ = 2.67 ± 0.01*D*

p-Fluorodiphenyl Sulfone

0.00316	0.8763	2.2563	2.2589	434.5	60.4
.00670	.8795	2.4502	2.2609	428.5	60.6
.00994	.8823	2.5355	2.2628	422.6	61.1
.01420	.8862	2.6484	2.2649	414.8	60.5

$_\infty P_2$ = 440.6; $_EP_2$ = 60.6; $_OP_2$ = 380.0 cc.; μ = 4.28 ± 0.02*D*

p,p'-Difluorodiphenyl Sulfone

0.00264	0.8760	2.3142	2.2483	285.0	61.4
.00409	.8776	2.3365	2.2589	281.0	60.6
.00506	.8787	2.3516	2.2593	279.8	59.8
.01025	.8840	2.4303	2.2615	274.6	60.4

$_\infty P_2$ = 287.0; $_EP_2$ = 60.5; $_OP_2$ = 226.5 cc.; μ = 3.31 ± 0.02*D*

p-Fluorobenzophenone

0.00364	0.8754	2.3108	2.2589	203.3	57.1
.00940	.8791	2.3721	2.2623	202.5	57.3
.01724	.8838	2.4526	2.2662	198.7	56.9
.02640	.8891	2.5462	2.2708	195.9	57.0

$_\infty P_2$ = 205.3; $_EP_2$ = 57.1; $_OP_2$ = 148.2 cc.; μ = 2.67 ± 0.02*D*

p,p'-Difluorobenzophenone

0.00338	0.8757	2.2890	....	123.0	..
.00735	.8787	2.3087	2.2603	123.0	57.8
.01139	.8817	2.3281	2.2619	122.8	57.4
.01695	.8860	2.3556	2.2642	122.6	57.0

$_\infty P_2$ = 123.2; $_EP_2$ = 57.4; $_OP_2$ = 65.8 cc.; μ = 1.78 ± 0.02*D*

Diphenylamine

0.00543	0.8755	2.2844	2.2618	77.56	57.8
.01100	.8775	2.2983	....	79.99	..
.01741	.8801	2.3130	2.2716	79.59	57.6
.03164	.8856	2.3486	2.2810	80.92	56.4

$_\infty P_2$ = 79.8; $_EP_2$ = 57.3; $_OP_2$ = 22.5 cc.; μ = 1.04 ± 0.01*D*

p-Fluorodiphenylamine

0.00465	0.8758	2.2986	....	128.4	..
.00456	.8756	....	2.2597	...	55.2
.00990	.8786	2.3269	....	126.8	..
.01502	.8815	2.3532	2.2673	124.9	56.5

$_\infty P_2$ = 130.0; $_EP_2$ = 55.8; $_OP_2$ = 74.2 cc.; μ = 1.89 ± 0.01*D*

p,p'-Difluorodiphenylamine

0.00429	0.8763	2.3017	....	146.9	..
.00663	.8779	2.3177	2.2606	147.5	55.6
.01164	.8814	2.3494	2.2631	144.3	55.6

$_\infty P_2$ = 148.8; $_EP_2$ = 55.6; $_OP_2$ = 93.2 cc.; μ = 2.12 ± 0.01*D*

Phenyl-*p*-tolylamine

f_2	d^{25}_4	ϵ	n^2	P_2	$_EP_2$
0.00468	0.8748	2.2846	2.2610	88.04	62.6
.00642	.8754	2.2885	....	87.00	..
.01138	.8773	2.3017	2.2664	88.37	62.5
.01649	.8792	2.3158	....	89.42	..
.02096	.8809	2.3265	2.2748	88.75	63.0
.02800	.8834	2.3447	....	88.90	..

$_\infty P_2$ = 88.7; $_EP_2$ = 62.7; $_OP_2$ = 26.0 cc.; μ = 1.12 ± 0.01*D*

Di-*p*-tolylamine

0.00562	0.8754	....	2.2609	....	64.8
.00583	.8754	2.2848	....	86.11	..
.01003	.8772	2.2942	2.2636	86.58	64.0
.01748	.8797	2.3090	....	86.47	..
.02782	.8839	2.3267	2.2740	84.12	63.9

$_\infty P_2$ = 87.0; $_EP_2$ = 64.2; $_OP_2$ = 22.8 cc.; μ = 1.05 ± 0.01*D*

Phenyl-*p*-tolylnitrosamine

0.00566	0.8767	2.3799	2.2614	328.1	65.6
.01385	.8809	2.5352	2.2663	321.8	65.1
.02023	.8844	2.6571	2.2715	317.1	65.8

$_\infty P_2$ = 332.4; $_EP_2$ = 65.5; $_OP_2$ = 266.9 cc.; μ = 3.59 ± 0.01*D*

Di-*p*-tolylnitrosamine

0.00616	0.8767	2.4054	2.2614	369.5	70.1
.01365	.8806	2.5702	2.2670	364.8	70.7
.02114	.8846	2.7336	2.2728	357.1	71.1

$_\infty P_2$ = 375.2; $_EP_2$ = 70.6; $_OP_2$ = 304.6 cc.; μ = 3.83 ± 0.01*D*

p-Fluorotriphenylamine

0.00311	0.8756	2.2858	2.2609	129.8	85.4
.00601	.8779	2.2980	....	128.8	
.00836	.8796	2.3076	....	128.4	85.5[27]
.00993	.8807	2.3137	....	127.8	

$_\infty P_2$ = 130.6; $_EP_2$ = 85.5; $_OP_2$ = 45.1 cc.; μ = 1.47 ± 0.02*D*

Phenoxthine

0.00351	0.8759	2.2809	2.2605	80.93	60.4
.00739	.8787	2.2900	2.2641	80.67	60.1
.01026	.8807	2.2967	2.2670	80.68	60.2
.01717	.8857	2.3129	2.2736	80.65	60.1

$_\infty P_2$ = 80.8; $_EP_2$ = 60.2; $_OP_2$ = 20.6 cc.; μ = 1.00 ± 0.01[31]

Phenthiazine

0.00222	0.8751	2.2901	....	161.1	..
.00461	.8768	2.3088	2.2634	160.3	65.4
.00659	.8783	2.3246	2.2658	160.4	64.8
.00890	.8799	2.3419	2.2687	158.7	64.7

$_\infty P_2$ = 162.2; $_EP_2$ = 65.0; $_OP_2$ = 97.2 cc.; μ = 2.16 ± 0.02*D*

In Table I all the dipole moment data used in the discussion are collected together.

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(31) Higasi (*Sci. Papers Inst. Phys. Chem. Res.* (*Tokyo*), **38**, 331 (1941)) reported 1.09.

(32) deVries and Rodebush, THIS JOURNAL, **53**, 2888 (1931).

(33) Kadesch and Weller, *ibid.*, **63**, 1310 (1941).

(34) Cowley and Partington, *J. Chem. Soc.*, 1252 (1933).

(35) A. H. Warburton, private communication.

TABLE II

C–X–C ANGLES, INTERACTION MOMENTS NEGLECTED

	μ_0	μ_s	μ_T	X	θ[a]
I	Diphenyl ether	Fluorobenzene	*p*-Fluorodiphenyl ether	O	125°
	Diphenyl ether	Fluorobenzene	*p,p'*-Difluorodiphenyl ether	O	112°
II	Diphenyl sulfide	Fluorobenzene	*p*-Fluorodiphenyl sulfide	S	114°
	Diphenyl sulfide	Fluorobenzene	*p,p'*-Difluorodiphenyl sulfide	S	95°
III	Diphenyl sulfoxide	Fluorobenzene	*p,p'*-Difluorodiphenyl sulfoxide	SO	(90°)[b]
		Toluene	Di-*p*-tolyl sulfoxide		
IV	Diphenyl sulfone	Fluorobenzene	*p*-Fluorodiphenyl sulfone	SO_2	100°
	Diphenyl sulfone	Fluorobenzene	*p,p'*-Difluorodiphenyl sulfone	SO_2	104°
V	Benzophenone	Fluorobenzene	*p*-Fluorobenzophenone	CO	129°
	Benzophenone	Fluorobenzene	*p,p'*-Difluorobenzophenone	CO	131°
VI	Diphenylamine	Fluorobenzene	*p*-Fluorodiphenylamine	NH	113°[c]
			p,p'-Difluorodiphenylamine		
VII	Triphenylamine	Fluorobenzene	*p*-Fluorotriphenylamine	NC_6H_5	114°[d]

[a] The values of θ are derived from dipole moments based on an allowance for $_AP = 5\%_EP$. [b] Very sensitive to changes in the value of μ_0; 3.97 used for this calculation. [c] The angle ω, between the unsubstituted moment μ_0 and the perpendicular to the plane of the benzene rings,[1] is 16°. [d] The angle between the N-phenyl bond and the axis of symmetry in triphenylamine is $\phi = \cos^{-1}(\mu_T^2 - \mu_0^2 - \mu_s^2)/2\mu_0\mu_s$; $\sin \theta/2 = \sqrt{3/2} \sin \phi$, where θ is the C–N–C angle.

Discussion

From the preceding data, we evaluated the valence angles in diphenyl ether, sulfide, sulfoxide, sulfone, ketone, amine and in triphenylamine. In Table II are given the results when interactions between the central group and the substituent group or groups are ignored. In Table III are the angle values corrected for these, together with the interaction moments themselves. These will be discussed *seriatim.*

TABLE III

C–X–C ANGLES, CORRECTED FOR INTERACTION MOMENTS

		$d_1\mu_s = d_2\mu_s$		$d_1\mu_s = 2d_2\mu_s$	
$_AP = 5\%_EP$	X	θ	$d_2\mu_s$	θ	$d_2\mu_s$
Diphenyl ether	O	117°	0.11	115°	0.07
Diphenyl sulfide	S	106°	.17	103°	.12
Diphenyl sulfone	SO_2	93°	− .16	106°	.08
Benzophenone	CO	128°	− .06	132°	.04

The value of 115–117° calculated for ∠C–O–C in diphenyl ether is lower than the value 124 ± 5° obtained by Coop and Sutton[4] from measurements on bromo derivatives in the gas-phase, but agrees well with the value of 118 ± 3° ascribed by Maxwell, Hendricks and Mosley[36] from an electron diffraction investigation. The probable range may be given as 115–124°. This is distinctly greater than the values for ∠C–O–C in aliphatic compounds, *viz.*, 111 ± 4° in dimethyl ether[37] and 108° in 1,4-dioxane.[38] The earlier differentiation[3] between the aromatic and the aliphatic ethers is therefore confirmed and its explanation in terms of resonance may still be regarded as valid.

The value of 103–106° found for ∠C–S–C in diphenyl sulfide is also lower than the earlier value, 113 ± 3° from the dipole moments of the *p*-chloro- and *p*-methyl-derivatives.[3] Toussaint,[39] from an X-ray investigation of the *p,p'*-dibromo-derivative, has obtained a value 109.5 ± 0.5°. In aliphatic compounds, the values reported for ∠C–S–C are, in dimethyl sulfide 100°[40] and 100–110°,[41] in 1,4-dithian 100°,[38] in *sym*-trithian 106.5°,[38] and in α- and β-trithioacetaldehyde also 106.5°.[38] The angles in this case are not, therefore, clearly different in the aromatic and aliphatic compounds, so there is no conclusive evidence from this source for resonance between the normal structure for diphenyl sulfide and others with positive, tricovalent sulfur. Toussaint[39] reports, however, that the C–S distance is 1.75 Å., *i. e.*, that it is shorter than the sum of the covalent radii (1.81 Å.) and that it therefore indicates some resonance of the type mentioned.

The value for ∠C–S–C in diphenyl sulfoxide (Table II) cannot be regarded as accurate since it is very sensitive to the moment value taken for diphenyl sulfoxide itself.

That in diphenyl sulfone, of 93–106°, or more probably 100–104°, is in good agreement with the 100° reported by Toussaint[39] from an X-ray diffraction examination of the *p,p'*-dibromo-derivative, though less than the 109° reported by Bergmann and Tschudnowsky.[42] Toussaint's value for the C–S distance is 1.84 Å., which should be compared with that of 1.90 Å. found by Lister and Sutton[43] in dimethyl sulfone. There is, therefore, some evidence of conjugation between the phenyl groups and the SO_2-group. Toussaint observes that the benzene rings are turned into planes at right angles to the C–S–C plane, but Koch[44] has

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(36) Maxwell, Hendricks and Mosley, *J. Chem. Phys.*, **3**, 699 (1935).

(37) Sutton and Brockway, THIS JOURNAL, **57**, 473 (1935).

(38) Hassel and Viervoll, *Acta Chemica Scandinavica*, **1**, 149 (1947).

(39) Toussaint, *Bull. soc. chim. Belg.*, **54**, 319 (1945).

(40) Pai, *Indian J. Phys.*, **9**, 121 (1934).

(41) Brockway and Jenkins, THIS JOURNAL, **58**, 2036 (1936).

(42) Bergmann and Tschudnowsky, *Ber.*, **65**, 457 (1932).

(43) Lister and Sutton, *Trans. Faraday Soc.*, **35**, 495 (1939).

(44) Koch, private communication.

TABLE IVa

CALCULATED ANGLE AND MOMENT VALUES FOR COMPOUNDS OF TYPE I

	α		0°	5	10	15	20	25	30	35
	180–2α		180°	170	160	150	140	130	120	110
	β		120°	119	117	113.5	109	103.5	97	90.5
	ω		0°	8.5	17	24	30.5	36	41	45
	X	Y								
$\mu_{\text{calcd.}}$	O	O	0	0.32	0.65	0.90	1.13	1.30	1.44	1.56
	O	S	0.34	0.53	0.83	1.10	1.35	1.54	1.70	1.83
	S	S	0	0.46	0.87	1.19	1.49	1.71	1.92	2.10
	S	NH	1.75	1.86	2.00	2.08	2.15	2.20	2.24	2.28
	Se	Se	0	0.42	0.80	1.12	1.39	1.60	1.82	1.92
	Te	Te	0	0.33	0.66	0.94	1.17	1.35	1.50	1.61

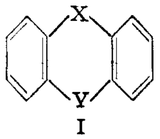
suggested that this need not necessarily preclude resonance between them and the SO_2-group.

The large angle, 128–132°, calculated in benzophenone agrees with that of 131–133° derived by Sutton and Hampson[3] (*cf.*, however, Coomber and Partington,[45] who consider 125 ± 3° to be more accurate, from considerations of interaction), and with the 135° reported by Banerjee and Jaque.[46] It is a clear indication that there is resonance involving structures with double bonds between the benzene rings and the carbonyl group.

The value of 113° for ∠C–N–C found in diphenylamine and that of 114° in triphenylamine are probably real, and they are larger than the value observed in trimethylamine, 108 ± 4°, by Brockway and Jenkins.[41] The inference is that, in accordance with the expectations of current theory, there is resonance involving structures with the grouping $\overset{+}{=}\mathrm{N}\!<$, but that neither molecule is coplanar.

Some moment values for N-nitrosodiphenylamino compounds were determined (Table I) in the hope that this group might be sufficiently rigid for the treatment applicable to diphenylamine to be suitable. The C–N–C angle calculated is, however, unreal, so the configuration of the N-nitroso group is evidently not simple. It is interesting to note that phenyl-*p*-tolylnitrosamine has a moment 3.59 D nearly equal to that of N-nitrosomethylaniline (3.62 *D*).[34]

The moments of molecules of type I have been measured by various authors and have been discussed in relation to the folding of the molecule along the X-Y line.[3,31,42,47,48,49,50] It is possible to show that the moments calculated when X = Y are close to those observed if it be assumed that the angle C–X–C is approximately the same in these compounds as in C_6H_5–X–C_6H_5, that the moments of the C–X–C segments are likewise equal to those of the diphenyl compound, and that the valences of carbon in the benzene rings are all coplanar and at 120° to each other.[47,50] This treatment may be extended to the case where X ≠ Y by taking a common mean value for both angles.



I

TABLE IVb

OBSERVED MOMENT VALUES IN COMPOUNDS OF TYPE I

X	Y	$\mu_{\text{obs.}}$			
O	O	0.64[50]	0[51]		
O	S	0.92[52]	1.09[50]		
S	S	1.68[42]	1.41[53]	1.54[54]	1.57[47]
S	NH	2.13[52]			
Se	Se	1.41[47]			
Te	Te	...			

In Table IVa, β is the angle C–X–C or C–Y–C in the tricyclic compound, 2α is the supplement of the angle between the benzene ring planes, ω is the angle between the C–X–C (or C–Y–C) segment and the X–Y line; $\mu_{\text{calcd.}}$ is the moment evaluated on the preceding assumptions for various values of β. For the particular case of phenthiazine, we assumed that ω is 90° for the C–NH–C segment. In Table IVb, the observed values ($\mu_{\text{obs.}}$) are given.

By comparison of these two tables, we see that agreement between calculated and observed values of the moments is obtained for the following values of β:

TABLE V

X	Y	β	180–2α
O	O	117–120°	160–180°
O	S	113–116°	150–160°
S	S	107–109°	135–140°
S	NH	109–113°	140–150°
Se	Se	107–109°	135–140°

Exact agreement between these β values and the valency angles in Table III would not be ex-

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(45) Coomber and Partington, *J. Chem. Soc.*, 1444 (1938).

(46) Banerjee and Jaque, *Indian J. Phys.*, **12**, 87 (1938).

(47) Campbell, LeFèvre, LeFèvre and Turner, *J. Chem. Soc.*, 404 (1938).

(48) Higasi and Uyeo, *J. Chem. Soc. Japan*, **62**, 396 (1941).

(49) Higasi and Uyeo, *ibid.*, **62**, 400 (1941).

(50) Higasi, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **38**, 331 (1941).

(51) Bennett, Earp and Glasstone, *J. Chem. Soc.*, 1179 (1934).

(52) This paper.

(53) Smyth and Walls, *J. Chem. Phys.*, **1**, 337 (1933).

(54) Bennett and Glasstone, *J. Chem. Soc.*, 128 (1934).

TABLE VI

INTERACTION MOMENTS[a]

p-Substituted	F	Cl	Br	I	NO_2
Toluenes	−0.14	−0.01	+0.04	+0.01	+0.07
Phenols	− .17	− .03	− .09	....	+0.71
Anisoles	− .06	+ .04	+ .15	+ .16	+0.37
Anilines[b]	− .17	+ .22	+ .20	+ .36	+1.26
Dimethylanilines	− .17	+ .34	+ .46	+ .69	+1.86
Nitrobenzenes	− .14	+ .05	− .02	+ .02	....
Benzaldehydes[45]	(− .27	− .25			+0.16)
Diphenyl ethers[c]	0.07 to 0.11	....	0.43 to 0.50[4]	....	0.70 to 0.76[3]
Diphenyl sulfides[c]	.12 to .17	0.10 to 0.16[3] +0.25[39]	+0.35[39]	....	....

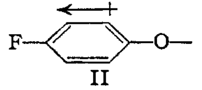
[a] Calculated by the method of Marsden and Sutton.[5] A negative value is one with its negative end away from the halogen atom. Moment values derived from the "Table of Dipole Moments" of Sidgwick and collaborators (*Trans. Faraday Soc.*, **30**, 1934) are: for toluene, 0.40; phenol, 1.61; aniline ($\theta_2 = 56°$), 1.53; anisole ($\theta_2 = 76°$), 1.23; dimethylaniline ($\theta_2 = 38°$), 1.58; nitrobenzene, 3.95; chlorobenzene, 1.56; bromobenzene, 1.52; iodobenzene, 1.30. [b] Series of Marsden and Sutton[5] recalculated. [c] Calculated simultaneously with bond angles.

pected, because the conditions which determine them are somewhat different in the two cases. The value which we derive for 180-2α in thianthrene, *ca.* 140°, is the same as that reported by Wood and Crackston,[55] from X-ray investigations. We find that 180-2α in selenanthrene also is *ca.* 140°, a value which agrees with the earlier one of Wood and Crackston, but which is higher than the revised one of 127° given by Wood and Williams.[56]

The phase-rule investigations made by Cullinane and Plummer[57] agree with there being a marked difference of configuration between diphenylene dioxide on the one hand and either thianthrene or selenanthrene on the other; likewise, Cullinane and Rees[58] find evidence of a difference between diphenylene dioxide and phenoxthine and a similarity between phenoxthine and phenthiazine.

The interaction moments between the substituent atoms and the central atoms in the ether and sulfides are perhaps less when fluorine is used (Table III) than when chlorine is used (Table VI), and, as expected, they are certainly less than with bromine. The sign of the interactions is such as to indicate that when fluorine is substituted *para* to the phenoxy group, the mesomeric moment of the former is diminished (see diagram II). According to the sign convention adopted (see Table VI) this is termed a positive change.

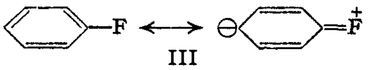
Examination of the interaction moments of halogens with other groups in *para* positions shows that they are less positive (using the preceding convention) the less polarizable the halogen, and are actually negative for fluorine. Therefore, although there is a difference between the actual sign for the interaction moments in the fluoro-substituted diphenyl ethers or sulfides and those in the other fluoro compounds listed, the algebraic changes in these moments, as the polarizability of the halogen increases, are the same.



II

Groves and Sugden[59] showed that the mesomeric effect of the fluorine atom is such that it drives electrons into the benzene ring and that it does this to a greater extent than does any other halogen. Our results show that fluorine has unique power to suppress the mesomeric effect of groups *para* to it if they conflict with its own.

This mesomeric effect of fluorine with benzene has been attributed to resonance between the structure with neutral monovalent fluorine and others with positive divalent fluorine (III) (*vide, e. g.*, Kenner[60]). In view of the great electronegativity of fluorine and its unwillingness to form single dative bonds, some doubts have been expressed about the validity of this explanation.[61] We suggest that an alternative should be considered, in which it is not necessary to postulate a change in multiplicity of the C–F bond, nor a positive charge on fluorine. The general problem is to discover the most stable state possible for the whole molecule, and this means discovering the most favorable electron distribution. It seems improbable that this will involve a considerable reduction in electron density around the fluorine atom; rather the reverse. Now, if we suppose that the key to the problem is that the electron density around the fluorine atom shall be increased, it is possible to propose a means by which this may happen, by which the C–F bond may be shortened and strengthened, and by which electrons may be driven into the benzene ring.



III

The carbon and fluorine atoms have some permitted range of atomic orbitals available for bond

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(55) Wood and Crackston, *Phil. Mag.*, **31**, 62 (1941).

(56) Wood and Williams, *Nature*, **150**, 321 (1942).

(57) Cullinane and Plummer, *J. Chem. Soc.*, 63 (1938).

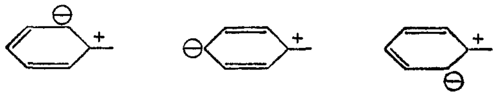
(58) Cullinane and Rees, *Trans. Faraday Soc.*, **36**, **507** (1940).

(59) Groves and Sugden, *J. Chem. Soc.*, **1992** (1937).

(60) Kenner, *Proc. Roy. Soc.* (*London*), **185A**, 119 (1946).

(61) Bennet, *J. Chem. Soc.*, 1112 (1933).

formation. These would vary in the degree of overlap which they would give in the bond, and therefore in the concentration of the negative cloud charge which they would give between the nuclei. At large internuclear distances, the orbitals giving greatest overlap would be least favored because they would require the removal of the negative centroid somewhat from each nucleus. If, however, either or both the atoms have high electronegativities, the high axial concentration resulting from these orbitals would increase stability, because the positive nuclei would be better shielded from each other, *i. e.*, the nuclei would be better "cemented" together, so they could approach more closely, the electrostatic potential energy of the system would be reduced, and accordingly, the total energy would also be lowered. There might, in fact, be opposing tendencies: on the one hand, for the electrons to remain held in the configurations which are best in the fields of the separate nuclei, and on the other hand, for them to move from these into others that are most favorable in the joint, binuclear field. We think it possible that in the C–F link a considerable degree of such redistribution might occur, with the results indicated, *viz.*, a shortening and strengthening of the C–F bond and a reduction in its dipole moment. Furthermore, if the bond shortens, the density of electronic charge on the carbon atom might actually increase, with the result that electronic distributions in the neighborhood might be repelled; *i. e.*, driven into the nucleus. If this field effect occurs by resonance with polar structures (IV) (as has previously been postulated[62]) the appearance of *o,p*-direction in fluorobenzene might be expected.


IV

Summary

The valence angles (C–X–C) in diphenyl ether, sulfide, sulfone, ketone, amine and in triphenylamine have been determined from the dipole moments in benzene solution of the unsubstituted and the *p*-fluoro-substituted compounds. They are, in the same order: 116 ± 4°, 106 ± 4°, 102 ± 4°, 130 ± 4°, 113 ± 3° and 114 ± 3°. The relation of these to other reported values, and their significance, have been discussed.

The moments of phenoxthine and phenthiazine have also been measured. They are 0.92 and 2.13 *D*, respectively. These agree with angles of 155 ± 5° and 145 ± 5° between the planes of the benzene rings, the molecules being folded along the OS and NS lines.

The moments resulting from the interaction between fluorine atoms substituted on benzene, with other groups *para* to them, show that fluorine has unique power to suppress mesomeric effects which conflict with its own.

The origin of the mesomeric effect in fluorobenzene has been discussed.

(62) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939, p. 141.

URBANA, ILLINOIS RECEIVED AUGUST 18, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

Search for Elements 94 and 93 in Nature. Presence of 94^{239} in Pitchblende[1]

BY GLENN T. SEABORG AND MORRIS L. PERLMAN[1a]

The discovery[2] of a rather easily prepared form of radioactive element 94 and the subsequent determination of the chemical properties[3] of 94 with the help of this isotope as tracer make it possible to conduct a search for 94 in natural minerals. It is convenient to search for 93, whose chemical properties[3,4] are also known, at the same time. The hope would be to discover a very long-lived 94 or 93 and that this be present in an amount large enough so that useful quantities chould be extracted from the minerals. Alpha and beta radioactivity is to be tested for in the final very thin sample which, in view of the chemical procedure, would contain the 94 or 93. In case the 94 or 93 is not alpha or beta active, a test for fissions with neutrons should be made since it appears likely that any isotopes of these elements will undergo fission either with slow or with fast neutrons. The presence of an amount of the order of one microgram can be established by the neutron tests; therefore, starting with about 1 lb. of the pitchblende, the sensitivity for the detection of these elements can be about 1 part in 10^8 or 10^9.

This report describes a careful search for elements 94 and 93 in a sample of pitchblende concentrate obtained from the Great Bear Lakes region of Canada. Since this pitchblende, which is

(1a) Now at the Research Laboratory of the General Electric Company at Schenectady, New York.

(1) This article was mailed, as a secret report, from Berkeley, California, to the "Uranium Committee" in Washington, D. C., on April 13, 1942. The experimental work was done during 1941 and the early part of 1942. The report is unchanged from its original form except for slight editing to make it conform to JOURNAL standards.

(2) G. T. Seaborg, E. M. McMillan, J. W. Kennedy and A. C. Wahl, *Phys. Rev.*, **69**, 366 (1946) (submitted January 28, 1941); G. T. Seaborg, A. C. Wahl and J. W. Kennedy, *Phys. Rev.*, **69**, 367 (1946) (submitted March 7, 1941).

(3) G. T. Seaborg and A. C. Wahl, THIS JOURNAL, **70**, 1128 (1948).

(4) E. M. McMillan and P. H. Abelson, *Phys. Rev.*, **57**, 1185 (1940).