

## 184. Dipole Moments of Substituted Phenoxyacetic Acids and Phenols.

By D. C. COLINESE, J. HALL, and D. A. IBBITSON.

Apparent dipole moments of a series of substituted phenoxyacetic acids and three additional *para*-substituted phenols have been determined from measurements on dilute solutions in dioxan at 25°. Interaction moments ( $\mu_{\text{int}}$ ) along the O-C (ring) bond necessary to correlate the observed and calculated moments have been evaluated, and in both the acid and phenol series they show a trend parallel with  $pK_a$  values. No correlation exists between either  $\mu_{\text{int}}$  or  $pK_a$  and the corresponding plant growth-regulating activity of the acids, although the latter property increases with increasing dipole moment of the acid molecule.

THE plant growth-regulating activity of an aryloxyalkylcarboxylic acid depends on the pH of plant tissues<sup>1,2</sup> and on the degree of dissociation of the acid.<sup>3</sup> It has been suggested that association occurs between active groups in the acid molecule and specific receptor sites in the plant cellular boundary.<sup>4</sup> If this interaction is physicochemical in nature, the dipole moment and the dissociation of the acid might be expected to be related to the extent of interaction between donor and receptor groups. This investigation has been carried out to assess these relationships.

Apparent dipole moments of eight phenoxyacetic acids and three monosubstituted phenols in dioxan have been determined; in both series  $pK_a$  values show a parallel trend with interaction moments,  $\mu_{\text{int}}$ , calculated along the O-C (ring) bond. Plant growth-regulating activity increases with increasing dipole moment of the acid molecule, but from the limited results obtained it is considered hazardous to attach significance to this observation.

### EXPERIMENTAL

*Materials.*—Phenoxyacetic acid, m. p. 99.0°, *p*-chloro-, m. p. 156.0°, *p*-bromo-, m. p. 157.5°, *p*-methyl-, m. p. 138.0°, 2,4,6-trichloro-, m. p. 182.5°, and 2,4,6-trimethyl-phenoxyacetic acid, m. p. 151.0°, were prepared by heating the corresponding recrystallised or redistilled phenol with chloroacetic acid, sodium hydroxide, and water, in the molar proportions 1:1:2:7, under reflux for 0.5—3 hr. Hydrochloric acid was added to precipitate the crude acid, which was then distilled in steam for 0.5—3 hr. to remove unchanged phenol and recrystallised from ethanol-water to constant m. p.

2,4,6-Tribromophenoxyacetic acid was prepared by distilling 2,4,6-tribromophenol (0.1 mole) with sodium ethoxide solution (0.1 g.-atom of sodium) under reduced pressure, and heating the solid residue with ethyl chloroacetate (0.1 mole). Hydrolysis of the ethyl ester by sodium hydroxide in ethanol-water, followed by acidification, gave the acid, m. p. 200.0° (from ethanol-water). 2,4-Dichlorophenoxyacetic acid was purchased, recrystallised from ethanol-water, and had m. p. 140.0°.

*p*-Fluoro-, *p*-cyano-, and *p*-nitro-phenol were prepared and recrystallised as described previously.<sup>5</sup> Dioxan and benzene were repeatedly refluxed with sodium and then fractionally distilled under anhydrous conditions.

*Method and Results.*—Dielectric constants and refractive indices of solutions of graded concentration of each compound in dioxan were determined at 25°. The apparatus and methods used were the same as in a previous investigation,<sup>6</sup> and the results are summarised in Table 1, where the symbols have their usual significance.

<sup>1</sup> Went and Thimann, "Phytohormones," Macmillan, London, 1937.

<sup>2</sup> Van Overbeek, *Ann. Rev. Plant Physiol.*, 1952, **3**, 87.

<sup>3</sup> Brian and Rideal, *Biochem. Biophys. Acta*, 1952, **9**, 1.

<sup>4</sup> Wain, "Plant Growth Substances," Royal Inst. Chem. Monograph No. 2, 1953.

<sup>5</sup> Goode and Ibbitson, *J.*, 1960, 4265.

<sup>6</sup> Erić, Goode, and Ibbitson, *J.*, 1960, 55.

The molar orientation polarisation at infinite dilution,  $P_{2\infty}$ , and the dipole moment,  $\mu$ , of each compound were calculated from equations (1) and (2), respectively:

$$P_{2\infty} = 3M_2v_1[\alpha/(\epsilon_1 + 2)^2 - \nu/(n_1^2 + 2)^2] \quad (1)$$

$$\mu = 0.012812(P_{2\infty}T)^\dagger, \quad (2)$$

TABLE 1.\*

100w	$\epsilon$	$n_D$	100w	$\epsilon$	$n_D$	100w	$\epsilon$	$n_D$	100w	$\epsilon$	$n_D$
Phenoxyacetic acid			<i>p</i> -Chlorophenoxyacetic acid			<i>p</i> -Bromophenoxyacetic acid			2,4-Dichlorophenoxyacetic acid		
0.000	2.2126	1.4205	0.000	2.2129	1.4202	0.000	2.2140	1.4205	0.000	2.2147	1.4202
0.100	2.2175	—	0.100	2.2206	—	0.111	2.2202	—	0.089	2.2205	—
0.293	2.2268	1.4209	0.310	2.2365	1.4207	0.309	2.2317	—	0.280	2.2333	—
0.435	2.2340	—	0.497	2.2505	—	0.495	2.2421	—	0.476	2.2462	—
0.600	2.2420	—	0.690	2.2659	1.4213	0.698	2.2535	—	0.666	2.2592	1.4210
0.673	2.2455	1.4213	0.987	—	1.4217	0.881	2.2638	—	1.383	—	1.4219
0.927	—	1.4217	1.370	—	1.4222	1.318	—	1.4220	2.360	—	1.4231
1.505	—	1.4224	1.630	—	1.4226	1.943	—	1.4227	3.494	—	1.4245
						2.592	—	1.4235			
2,4,6-Trichlorophenoxyacetic acid			2,4,6-Tribromophenoxyacetic acid			2,4,6-Trimethylphenoxyacetic acid			<i>p</i> -Tolyloxyacetic acid		
0.000	2.2141	1.4198	0.000	2.2120	1.4202	0.000	2.2111	1.4202	0.000	2.2122	1.4199
0.096	2.2172	—	0.096	2.2147	—	0.099	2.2153	—	0.097	2.2167	—
0.195	2.2203	—	0.219	2.2185	—	0.198	2.2197	—	0.290	2.2262	—
0.384	2.2263	—	0.400	2.2238	—	0.389	2.2280	—	0.482	2.2354	—
0.580	2.2323	—	0.578	2.2290	—	0.581	2.2364	—	0.674	2.2448	—
1.600	—	1.4213	1.087	—	1.4214	0.959	—	1.4212	0.864	2.2540	1.4208
2.532	—	1.4222	1.900	—	1.4224	1.939	—	1.4222	1.830	—	1.4218
3.850	—	1.4234	2.235	—	1.4228	2.845	—	1.4232	2.500	—	1.4225
			3.261	—	1.4239				3.190	—	1.4232
<i>p</i> -Cyanophenol			<i>p</i> -Nitrophenol			<i>p</i> -Fluorophenol					
0.000	2.2100	1.4197	0.000	2.2127	1.4198	0.000	2.2093	1.4199			
0.034	2.2193	—	0.057	2.2275	—	0.162	2.2222	—			
0.080	2.2331	—	0.115	2.2434	—	0.420	2.2436	—			
0.106	2.2408	—	0.165	2.2562	—	0.550	2.2540	—			
0.145	2.2523	—	0.248	2.2782	—	0.654	2.2625	—			
0.185	2.2643	—	0.398	2.3176	—	0.771	2.2718	—			
0.790	—	1.4209	1.031	—	1.4216	0.885	—	1.4207			
2.480	—	1.4237	2.835	—	1.4246	3.020	—	1.4225			
4.430	—	1.4266	4.825	—	1.4279	4.684	—	1.4239			

\* All compounds in dioxan.

where  $M_2$  = molecular weight of compound,  $v_1$ ,  $\epsilon_1$ ,  $n_1$ , are the specific volume, dielectric constant, and refractive index, respectively, of dioxan at 25°;  $\alpha = (d\epsilon/dw)_{w=0}$ ,  $\nu = (dn^2/dw)_{w=0}$ .  $\alpha$  and  $\nu$  were determined from the limiting slopes of the plots of  $\epsilon$  against  $w$ , and of  $n_D^2$  against  $w$ .

## DISCUSSION

Polarisation data are summarised in Table 2.

TABLE 2.

Polarisation data.

Compound	$10^3\alpha$	$10^3\nu$	$P_{2\infty}$ (c.c.)	$\mu_D$ (D)
Phenoxyacetic acid	4867	37	111.6	2.34
<i>p</i> -Bromophenoxyacetic acid	5665	33	201.4	3.14
<i>p</i> -Chlorophenoxyacetic acid	7598	42	218.9	3.27
<i>p</i> -Tolyloxyacetic acid	4842	29	123.6	2.46
2,4-Dichlorophenoxyacetic acid	6646	35	227.4	3.33
2,4,6-Tribromophenoxyacetic acid	2968	33	166.7	2.86
2,4,6-Trichlorophenoxyacetic acid	3183	27	121.2	2.43
2,4,6-Trimethylphenoxyacetic acid	4355	30	128.7	2.51
<i>p</i> -Cyanophenol	29,250	46	563.8	5.25
<i>p</i> -Fluorophenol	8110	24	144.7	2.67
<i>p</i> -Nitrophenol	26,400	48	591.9	5.38

Goode and Ibbitson<sup>5</sup> determined the dipole moments of a series of *para*-substituted phenols in benzene, and calculated interaction moments along the O-C (ring) bond necessary to correlate the observed and the calculated moments. These interaction moments show a trend parallel with acid dissociation constants.

In the case of the substituted phenoxyacetic acids, interaction moments ( $\mu_{\text{int}}$ ) along the O-C (ring) bond have been calculated by two methods, and satisfactory agreement obtained.

In method (a), the angle which the C-O-CH<sub>2</sub>-CO<sub>2</sub>H group moment in phenoxyacetic acid makes with the O-C (ring) bond (74° 30') was determined vectorially from the moments of phenoxyacetic acid (2.34 D), *p*-bromophenoxyacetic acid (3.14 D), and bromobenzene (1.56 D), these moments being used because the  $pK_a$  values of phenoxyacetic acid and the *p*-bromo-derivative were found to be almost identical.  $\mu_{\text{int}}$  for these acids would then be zero. By taking the values chlorobenzene 1.58 D and toluene 0.37 D for the moments of the parent monosubstituted benzenes ( $\mu_{\text{PhX}}$ ), the dipole moments ( $\mu_{\text{calc}}$ ) of the *para*-substituted phenoxyacetic acids have been calculated from equation (3):

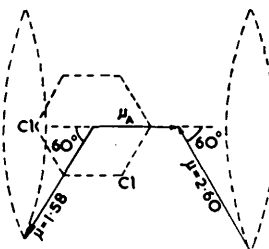
$$\mu_{\text{calc}}^2 = 2.34^2 + \mu_{\text{PhX}}^2 + 2(2.34)\mu_{\text{PhX}} \cos 74^\circ 30'. \quad (3)$$

Interaction moments along the O-C (ring) bond necessary to explain the observed dipole moments have been calculated from equation (4):

$$\mu_{\text{D}}^2 = 2.34^2 + (\mu_{\text{PhX}} + \mu_{\text{int}})^2 + 2(2.34)(\mu_{\text{PhX}} + \mu_{\text{int}}) \cos 74^\circ 30'. \quad (4)$$

We assumed the Ph-O-C bond angle in the acids to be 120°<sup>7,8</sup> and calculated the moments  $\mu_{\text{PhO}}$  and  $\mu_{\text{O-CH}_2\text{-CO}_2\text{H}}$  acting along the O-C (ring) and O-CH<sub>2</sub> bonds in phenoxyacetic acid, by a method previously described,<sup>6</sup> to be 0.68 and 2.60 D, respectively, the

FIG. 1. Calculation of  $\mu_{\text{calc}}$  and  $\mu_{\text{int}}$  ( $= 0.68 - \mu_A$ ) for 2,4-dichlorophenoxyacetic acid [method (a)].



oxygen atom being at the negative end of each dipole.  $\mu_{\text{int}}$  for 2,4-dichlorophenoxyacetic acid was calculated from equation (5), by assuming free rotation of the two vectors about the O-C (ring) bond (Fig. 1), and  $\mu_{\text{calc}}$  by putting  $\mu_{\text{int}}$  equal to zero in equation (5):

$$\mu_{\text{D}}^2 = [2.60 \cos 60^\circ + 1.58 \cos 60^\circ - (0.68 - \mu_{\text{int}})]^2 + (2.60^2 \sin^2 60^\circ + 1.58^2 \sin^2 60^\circ). \quad (5)$$

$\mu_{\text{calc}}$  and  $\mu_{\text{int}}$  values are recorded in Table 3.

Comparison of the moments of monomeric acetic acid in benzene<sup>9</sup> (1.68 D), in dioxan<sup>10</sup> (1.74 D), and in the vapour state<sup>11</sup> (1.73 D), suggests that the solvent effect in dioxan is small, possibly because the hydrogen bond between the acid and dioxan is nearly perpendicular to the direction of the resultant carboxyl group moment,<sup>12</sup> so that any effect on the resultant group moment created by the hydrogen bond is considerably minimised. In method (b), therefore, assuming that interaction between phenoxyacetic acid and dioxan is similarly small, that the carboxyl group is in the *trans*-configuration, and that the

<sup>7</sup> Anzilotti and Curran, *J. Amer. Chem. Soc.*, 1943, **65**, 607.

<sup>8</sup> Smith, "Electric Dipole Moments," Butterworths Scientific Publns., London, 1955, p. 245.

<sup>9</sup> Pohl, Hobbs, and Gross, *J. Chem. Phys.*, 1941, **9**, 408.

<sup>10</sup> Wilson and Wenzke, *J. Chem. Phys.*, 1934, **2**, 546.

<sup>11</sup> Zahn, *Phys. Rev.*, 1931, **37**, 1516.

<sup>12</sup> Bates and Hobbs, *J. Amer. Chem. Soc.*, 1951, **73**, 2151.

O-CH<sub>2</sub>-C bond angle in phenoxyacetic acid is 110°, we have calculated the moment  $m_1$  of the CH<sub>2</sub>·CO<sub>2</sub>H unit (1.77 D at angle 33° 30' to the O-CH<sub>2</sub> bond) from the following bond angles and moments (Bates and Hobbs's assumed parameters in acetic acid<sup>12</sup> being given in parentheses): C-C=O, 124° (124°); O=C-O, 124° (124°); C-O-H, 110° (110°); H-O, 1.53 (1.5); C-O, 0.76 (0.9); C=O, 2.60 (2.4); H-C, 0.30 (0.4) (the direction of the dipole in each case being + →).

On the assumption that the C-O bond moment ( $m_2$ ) along the CH<sub>2</sub>-O axis is 0.88 D, the ether oxygen atom bond angle<sup>7,8</sup> is 120°, and rotation about the O-CH<sub>2</sub> axis is free,<sup>13</sup> the moment along the O-C (ring) bond ( $\mu_{\text{PhO}}$ ) necessary to explain the observed moment of phenoxyacetic acid has been calculated from equation (6) to be 0.58 D, the oxygen atom being at the negative end of the dipole:

$$2.34^2 = (1.77 \cos 33.5^\circ + 0.88 - \mu_{\text{PhO}} \cos 60^\circ)^2 + (\mu_{\text{PhO}} \sin 60^\circ + 1.77^2 \sin^2 33.5^\circ). \quad (6)$$

The assumption of a C-O bond moment ( $m_2$ ) of 0.88 D appears to be justified since it leads to a value  $\mu_{\text{PhO}} = 0.58$ , in agreement with  $\mu_{\text{PhO}}$  in anisole (0.58 D), as calculated by a

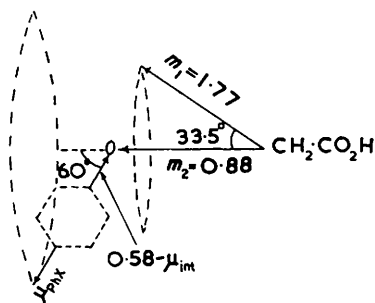


FIG. 2. Calculation of  $\mu_{\text{calc}}$  and  $\mu_{\text{int}}$  for *para*-substituted phenoxyacetic acids [method (b)].

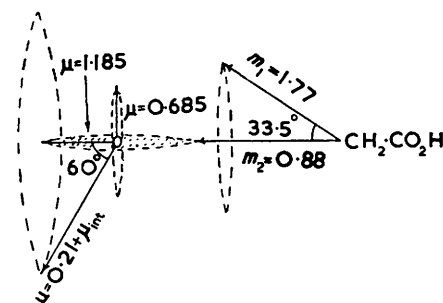


FIG. 3. Calculation of  $\mu_{\text{calc}}$  and  $\mu_{\text{int}}$  for 2,4-dichlorophenoxyacetic acid [method (b)].

method previously described<sup>6</sup> from the moments of anisole<sup>14</sup> ( $\mu = 1.30$  D), *p*-fluoroanisole<sup>15</sup> ( $\mu = 2.09$  D), and fluorobenzene<sup>15</sup> ( $\mu = 1.84$  D) in benzene, with the assumption of an oxygen atom bond angle<sup>8</sup> of 120°.

Interaction moments ( $\mu_{\text{int}}$ ) along the O-C (ring) bond, necessary to explain the observed acid dipole moments, have been calculated from equation (7) in which  $\mu_{\text{PhO}}$  is taken to be 0.58 D, and the moments of the corresponding monosubstituted benzenes ( $\mu_{\text{PhX}}$ ) are those used in method (a) (Fig. 2).  $\mu_{\text{calc}}$  was obtained by setting  $\mu_{\text{int}}$  equal to zero in equation (7).

$$\mu_{\text{D}}^2 = [1.77 \cos 33.5^\circ + 0.88 + (\mu_{\text{PhX}} + \mu_{\text{int}} - 0.58) \cos 60^\circ]^2 + [1.77^2 \sin^2 33.5^\circ + (\mu_{\text{PhX}} + \mu_{\text{int}} - 0.58)^2 \sin^2 60^\circ]. \quad (7)$$

In calculating  $\mu_{\text{int}}$  and  $\mu_{\text{calc}}$  for 2,4-dichlorophenoxyacetic acid, allowance has been made for free rotation of the *ortho* C-Cl dipole about the O-C (ring) bond as follows: (i) the C-Cl dipoles in positions 2 and 4 are replaced by a single dipole in position 3 with a moment of 1.58 D; (ii) resolved components of this single dipole along the O-C (ring) bond, and perpendicular to the same bond, are  $1.58 \cos 60^\circ = 0.79$  D, and  $1.58 \sin 60^\circ = 1.369$  D, respectively; (iii) the total moment along the O-C (ring) axis is  $0.79 + \mu_{\text{int}} - 0.58 = 0.21 + \mu_{\text{int}}$ ; and (iv) the vector  $1.369$  may be replaced by a vector  $1.369 \cos 30^\circ = 1.185$  rotating in a plane parallel to the O-CH<sub>2</sub> axis, and a vector  $1.369 \sin 30^\circ = 0.685$  rotating in a plane perpendicular to the O-CH<sub>2</sub> axis (Fig. 3).

<sup>13</sup> Fuchs, *Z. phys. Chem.*, 1931, B, 14, 339.

<sup>14</sup> Le Fèvre and Le Fèvre, *J.*, 1950, 1830.

<sup>15</sup> Ref. 8, p. 209.

$\mu_{\text{int}}$  was calculated from equation (8), in which allowance has been made for the four rotating vectors.  $\mu_{\text{calc}}$  was obtained by setting  $\mu_{\text{int}}$  equal to zero in equation (8):

$$3.33^2 = \{[1.77 \cos 33.5^\circ + 0.88 + (0.21 + \mu_{\text{int}}) \cos 60^\circ]^2 + (1.185)^2\} \\ + [1.77^2 \sin^2 33.5^\circ + (0.685)^2 + (0.21 + \mu_{\text{int}})^2 \sin^2 60^\circ]. \quad (8)$$

$\mu_{\text{int}}$  values are summarised in Table 3.

Considerable evidence exists that the effects of ring substituents on the ionisation of aromatic acids are additive.<sup>16</sup> Although steric hindrance may occur and affect acid strength in di- and tri-substituted phenoxyacetic acids, additivity was assumed and the calculated  $\text{p}K_{\text{a}}$  values recorded in Table 3 were obtained from the tabulated experimental  $\text{p}K_{\text{a}}$  data and Hayes and Branch's  $\text{p}K_{\text{a}}$  values: *o*-chlorophenoxyacetic acid 3.05, *o*-bromophenoxyacetic acid 3.12, *p*-bromophenoxyacetic acid 3.13, and 2,6-dimethylphenoxyacetic acid 3.36.

TABLE 3.

Interaction moments, calculated dipole moments, and  $\text{p}K_{\text{a}}$  values of substituted phenoxyacetic acids.

Subst.	Method (a)			Method (b)			$\text{p}K_{\text{a}}$	Growth activity <sup>a</sup>
	$\mu_{\text{D}}$	$\mu_{\text{calc}}$	$\mu_{\text{int}}$	$\mu_{\text{calc}}$	$\mu_{\text{int}}$	$\text{p}K_{\text{a}}$		
2,4,6-Me <sub>3</sub> .....	2.51	2.34	-1.73	2.34	-1.69	3.41 <sup>b</sup>		
<i>p</i> -Me .....	2.46	2.27	-1.24	2.27	-1.19	3.22 <sup>a</sup>		
H .....	2.34	2.34	0.00	2.34	0.00	3.17 <sup>a</sup>	I	
<i>p</i> -Br .....	3.14	3.14	0.00	3.13	0.02	3.13 <sup>a</sup>		
<i>p</i> -Cl .....	3.27	3.15	0.16	3.14	0.18	3.10 <sup>a</sup>	A	
2,4,6-Br <sub>3</sub> .....	2.86	2.34	1.13	2.34	1.15	3.03 <sup>b</sup>	A.I.	
2,4-Cl <sub>2</sub> .....	3.33	2.99	0.63	2.99	0.64	2.98 <sup>b</sup>	H.A.	
2,4,6-Cl <sub>3</sub> .....	2.43	2.34	0.28	2.34	0.29	2.86 <sup>b</sup>	A.I.	

I = Inactive, A.I. = Almost inactive, A = Active, H.A. = Highly active. <sup>a</sup> Hayes and Branch, *J. Amer. Chem. Soc.*, 1943, **65**, 1555. <sup>b</sup> Calculated values.

Table 3 shows that, in general,  $\text{p}K_{\text{a}}$  decreases with increase in  $\mu_{\text{int}}$ . Also it is apparent that no simple correlation exists between either  $\mu_{\text{int}}$  or  $\text{p}K_{\text{a}}$  and the corresponding plant growth-regulating activity, although the latter property increases with increasing dipole moment of the acid molecule.

From the results of a previous investigation,<sup>5</sup> it was considered of interest to calculate  $\mu_{\text{int}}$  for substituted phenols from dipole moments measured in dioxan. The angle which the C-O-H group moment makes with the O-C bond in phenol ( $74^\circ 25'$ ) was calculated vectorially from the moments of phenol <sup>6</sup> (1.86 D), *p*-fluorophenol (2.67 D), and fluorobenzene (1.48 D). These compounds were chosen for the calculation because the  $\text{p}K_{\text{a}}$

TABLE 4.

Interaction moments, calculated dipole moments, and  $\text{p}K_{\text{a}}$  values of substituted phenols.

Subst.	$\mu_{\text{D}}$ (D)	$\mu_{\text{calc}}$ (D)	$\mu_{\text{int}}$ (D)	$\text{p}K_{\text{a}}$	Subst.	$\mu_{\text{D}}$ (D)	$\mu_{\text{calc}}$ (D)	$\mu_{\text{int}}$ (D)	$\text{p}K_{\text{a}}$
H .....	1.86 <sup>a</sup>	1.86	0.00	9.99 <sup>b</sup>	<i>p</i> -F .....	2.67	2.67	0.00	9.95 <sup>f</sup>
<i>p</i> -Br .....	2.75 <sup>a</sup>	2.73	0.03	9.34 <sup>c</sup>	<i>p</i> -Me ...	1.83	1.80	-0.13	10.26 <sup>b</sup>
<i>p</i> -Cl .....	2.82 <sup>a</sup>	2.75	0.10	9.38 <sup>d</sup>	<i>p</i> -NO <sub>2</sub> ...	5.38	4.85	0.56	7.14 <sup>d</sup>
<i>p</i> -CN ...	5.25	4.87	0.40	7.95 <sup>e</sup>					

<sup>a</sup> Ref. 6. <sup>b</sup> Biggs, *Trans. Faraday Soc.*, 1956, **52**, 35. <sup>c</sup> Bordwell and Cooper, *J. Amer. Chem. Soc.*, 1952, **74**, 1058. <sup>d</sup> Judson and Kilpatrick, *ibid.*, 1949, **71**, 3110. <sup>e</sup> Wheland, Brownell, and Mayo, *ibid.*, 1948, **70**, 2492. Bennett, Brooks, and Glasstone, *J.*, 1935, 1821.

values of fluorophenol and phenol are almost identical. Values of  $\mu_{\text{calc}}$  and  $\mu_{\text{int}}$  were then obtained by a method previously described,<sup>5</sup> and the results together with relevant  $\text{p}K_{\text{a}}$  values are summarised in Table 4.

From a consideration of the data in Table 4,  $\text{p}K_{\text{a}}$  is seen to decrease almost linearly

<sup>16</sup> Braude and Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, 1955.

with increase in  $\mu_{\text{int}}$ . Also a given change in  $\mu_{\text{int}}$  arising from replacement of one *para*-substituent by another corresponds to a much greater change in  $\text{p}K_{\text{a}}$  value for the phenols than for the phenoxyacetic acids. In explanation it is suggested that because of the insulating effect of the  $\text{CH}_2$  group in the acids, the change in C-O bond moment ( $\mu_{\text{int}}$ ) will have a smaller effect on the polarity of the O-H bond in the carboxyl group than on that of the O-H bond in the phenols.

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DERBY AND DISTRICT COLLEGE OF TECHNOLOGY.

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