[CONTRIBUTION FROM THE SOLUTION CHEMISTRY SECTION, NATIONAL BUREAU OF STANDARDS, WASHINGTON 25, D. C.]

Comparison of the Relative Acidic Strengths of the Isomeric Dinitrophenols in Benzene and Water

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In earlier work the relative strengths of benzoic acid and numerous substituted benzoic acids were determined in benzene in terms of association with 1,3-diphenylguanidine, and the logarithms of the association constants were compared with corresponding pK_a values in water. The results gave insight into the role of chelation, solvation of the carboxyl group and solvation of other substituent groups in causing changes in the order of acidic strengths when water is replaced by a nonaqueous solvent. This paper reports a continuation of this type of study in which the relative strengths of all six of the isomeric dinitrophenols in benzene were determined at 25° in terms of association with triethylamine. The relationship of strengths in benzene and water is not a linear one. The results together with other available data point to anomalous behavior for 2,4-, 2,5- and 2,6-dinitrophenols, which is considered to be caused at least in part by a strong tendency for chelation between phenolic –OH and an *ortho*-nitro group. These three dinitrophenols have been used as acid–base indicators in aqueous and nonaqueous solvents. It seems desirable to seek out new acidic indicators in which a marked tendency toward chelation is absent.

Introduction

An effective way of judging solvent effects on electrolyte behavior is to make comparisons in amphiprotic and aprotic solvents. For acids, one may compare the relative pK_a values in water with the relative tendencies for combination with a reference base in a solvent such as benzene. This was illustrated in an earlier study[1] in which the relative strengths of benzoic acid and 39 substituted benzoic acids were measured in benzene in terms of association with the base diphenylguanidine, following which the logarithms of the association constants were compared with corresponding pK_a values in water. The results furnished insight into the role of factors such as chelation and solvation of substituent groups. As was to be expected, these factors proved to have greatest significance for substitutions *ortho* or *para* to the carboxyl group.

This paper reports the determination of the relative strengths of the six isomeric dinitrophenols in benzene at 25° in terms of association with triethylamine. The relative strengths in benzene are compared with the pK values of the dinitrophenols in aqueous solutions.[2]

In studies of acidic behavior, the phenols have not received attention commensurate with their importance. Much further work is needed to ascertain the influence of substituents and environmental conditions on their relative strengths and should lead to improvements and extensions of their use in analytical and other scientific applications.

2,4- and 2,6-dinitrophenols, commercially obtained, are used as acid–base indicators, especially the former, and 2,5-dinitrophenol is also used occasionally as an indicator. In recent years all three have been used as reference acids in studies of relative basicities in aprotic and other nonaqueous solvents.[3] It is important to discover to what extent results of such studies may be influenced by a tendency toward chelation of the *ortho*-nitro group with the phenolic –OH. In *o*-nitrophenol the presence of a stable six-membered chelate ring is considered to be well established for solutions in aprotic solvents,[4,5] and there is evidence of persistence of this structure in electron-donor solvents such as ethers.[4,5cd,6] A strong tendency toward chelation has also been reported for 2,4-dinitrophenol[5ad,7] and for 2,6-dinitrophenol.[5d,8] It should not be surprising to discover that manifestations of their acidic character vary with environmental conditions to a greater extent than in the case of 3,4- or 3,5-dinitrophenol.[9]

Experimental

Materials.—2,4- and 2,6-Dinitrophenols obtained commercially were crystallized from ethanol–water and benzene–cyclohexane, respectively. Melting points: 2,4-isomer, 113.1–113.7°; 2,6-isomer, 63.0–63.7°. The other dinitrophenols were synthesized and purified as already described.[3] Benzene and triethylamine were purified as in earlier work.[1,3d]

Apparatus and Method.—Experimental equipment, conditions and procedures were the same as (or closely similar to) those of previous studies.[3d] Concentrations of solutions used in absorbance measurements are indicated in Table II. At the low concentrations used measurable deviations from Beer's law were not expected. However, absorbance checks were made for 3,4- and 3,5-dinitrophenols, covering the molar concentration range 10^{-5} to 10^{-3}. Checks were also made for 2,3-, 2,4- and 2,5-dinitrophenols. No deviations from Beer's law were detected. Association constants are in the units liter mole^{-1} and correspond to the equation B(triethylamine) + A(dinitrophenol) $\rightleftarrows$ S(triethylam-

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[1] M. M. Davis and H. B. Hetzer, *J. Research Natl. Bur. Standards*, **60**, 569 (1958). The strengths were determined spectrophotometrically in the visible region, using bromophthalein magenta E (3',5',3",5"-tetrabromophenolphthalein ethyl ester) as the indicator.

[2] Thermodynamic pK_a values for four of the dinitrophenols in aqueous solutions have been determined in this Laboratory, using the materials prepared for this study. See R. A. Robinson, M. M. Davis, M. Paabo and V. E. Bower, *J. Research Natl. Bur. Standards*, **64A**, 347 (1960).

[3] For examples see (a) R. P. Bell and J. W. Bayles, *J. Chem. Soc.*, 1518 (1952); (b) J. W. Bayles and A. Chetwyn, *ibid.*, 2328 (1958); J. W. Bayles and A. F. Taylor, *ibid.*, 417 (1961); (c) R. G. Pearson and D. C. Vogelsong, *J. Am. Chem. Soc.*, **80**, 1038 (1958); (d) M. M. Davis and M. Paabo, *ibid.*, **82**, 5081 (1960).

[4] W. Gordy, *J. Chem. Phys.*, **7**, 167 (1939).

[5] Recent studies of this topic, with references to earlier literature, include: (a) P. M. Boll, *Acta Chem. Scand.*, **12**, 1777 (1958); (b) A. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **80**, 5358 (1958); (c) L. J. Bellamy and H. E. Hallam, *Trans. Faraday Soc.*, **55**, 220 (1959); (d) J. H. Richards and S. Walker, *ibid.*, **57**, 406 (1961); (e) J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **38**, 1837 (1960).

[6] Weak intramolecular hydrogen bonds may be favored over stronger intermolecular hydrogen bonds even in highly polar solvents because of the small magnitude of the entropy change accompanying their formation (see H. H. Jaffé, *J. Am. Chem. Soc.*, **79**, 2373 (1957)).

[7] J. A. Davison, *J. Am. Chem. Soc.*, **67**, 228 (1945).

[8] G. E. Hilbert, O. R. Wulf, S. B. Hendricks and U. Liddel, *ibid.*, **58**, 548 (1936).

[9] Chelation is almost certainly a factor in the markedly reduced strength of *o*-methoxybenzoic acid in benzene as compared with water (see ref. 1, section 4.2.*d*). Solvation of the nitro group seems likely to have most effect when it is *para* to the –OH group (*ibid.*, section 4.2.*c*).

TABLE I

OPTICAL CONSTANTS OF DINITROPHENOLS AND THEIR TRIETHYLAMMONIUM (Et_3NH) SALTS IN BENZENE AT 25°

	No base added		Et_3NH salt[a]		Isosbestic points	
Dinitrophenol	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}.	λ, mμ	ε
2,3	350	3700	425	3,500	382	1960
2,4	330 to 340[b]	3070	353	16,900	314	4400
			390 to 400[b]	8,500		
2,5	365	3490	455	5,000	320	2470
					397.5	1750
2,6	350	4400	435	8,650	378	2300
3,4	280?	5700?	320 to 340[c]	5800 to 6900	307	4700
			375	9,300		
3,5	335	2840	350	2,500	295	1960
					344	2350

[a] Solutions of the dinitrophenol containing a large excess of triethylamine were used. [b] Step-out. [c] Shoulder.

monium dinitrophenolate). The symbols C_a, etc., refer to stoichiometric concentrations; symbols enclosed in brackets apply to equilibrium concentrations deduced from absorbance data and the stoichiometry. The association constants are based on data for at least two wave lengths. When feasible, the wave lengths selected were near maxima for both the free acid and its triethylammonium salt.

Results

Addition of triethylamine to benzene solutions of the isomeric dinitrophenols causes characteristic shifts of the absorption to longer wave lengths. Except in the cases of 2,3- and 3,5-dinitrophenols, there is an accompanying increase in intensity of absorption. Positions and intensities of the absorption bands before and after the addition of triethylamine, and also the positions of isosbestic points, are summarized in Table I. The association constants obtained are summarized in Table II, which also indicates the range of concentrations and the precision of the results. The precision and the conformance of the reaction to the simple equation postulated are more readily apparent from Fig. 1. In constructing Fig. 1, results for only one wave length were used (see Table II, footnote *a*). The wave lengths selected were those for which the results were thought to be the best or for which data were a little more extensive. However, the results for different wave lengths agreed so well that inclusion of all the data would have made hardly any perceptible difference in the figure.[10–12]

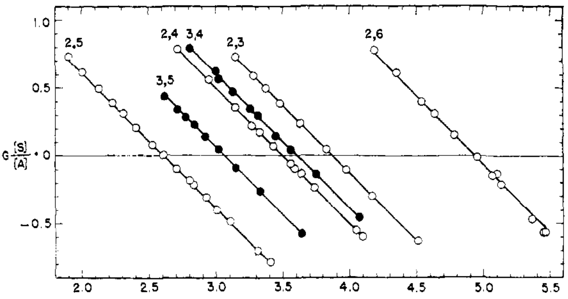

Fig. 1.—Graph constructed from spectral absorbance data and stoichiometric concentrations for mixtures of triethylamine with the isomeric dinitrophenols in benzene at 25°. The reaction assumed is addition of base and acid, forming a salt consisting of hydrogen-bonded ion-pairs. Symbols enclosed in brackets signify equilibrium concentrations of acid, base and salt. For wave lengths of measurements see footnote [a] of Table II.

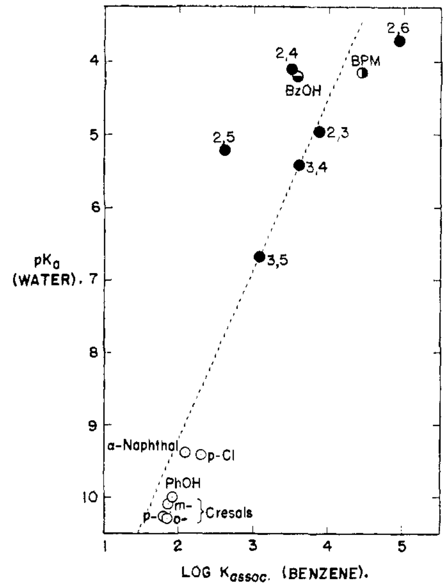

Fig. 2.—Comparison of the strengths of phenols in benzene and water at 25°, as measured by log $K_{assoc.}$ and pK_a, respectively, where log $K_{assoc.}$ applies to the reaction B (triethylamine) + HA (a phenol) $\rightleftarrows BH^+ \ldots A^-$. The six filled circles apply to experiments in which HA was one of the isomeric dinitrophenols; BPM signifies that the phenol was bromophthalein magenta E; BzOH signifies that HA was benzoic acid. The open circles were located using $K_{assoc.}$ values from other laboratories: When HA was phenol or α-naphthol the solvent was heptane, and when HA was a cresol or *p*-chlorophenol, the solvent was cyclohexane and the base was *trimethylamine* (for further particulars see Table III).

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(10) The diagonals in Fig. 1 all have the slope −1 and were placed so as to intersect the horizontal line where log ([S]/[A]) equals 0 at the points where −log [B] has the same value as the logarithm of the $K_{assoc.}$ value adopted (see last column of Table II).

(11) The triethylammonium salts of the dinitrophenols are considered to exist in benzene as hydrogen-bonded ion-pairs, for reasons analogous to those previously discussed. See (a) M. M. Davis and P. J. Schubmann, *J. Research Natl. Bur. Standards*, **39**, 221 (1947); (b) M. M. Davis and E. A. McDonald, *ibid.*, **42**, 595 (1949); (c) M. M. Davis and M. Paabo[3d]; (d) M. M. Davis and H. B. Hetzer, *J. Research Natl. Bur. Standards*, **65A**, 209 (1961).

(12) In some analogous studies employing tribenzylamine as the reference base, rapid, spontaneous formation of tribenzylamine oxide, in very small but readily detectable amounts, occurred (M. M. Davis and H. B. Hetzer, *J. Am. Chem. Soc.*, **76**, 4247 (1954)). The acid–

TABLE II

EQUILIBRIUM CONSTANTS FOR ASSOCIATION OF THE SIX DINITROPHENOLS WITH TRIETHYLAMINE IN BENZENE AT 25°[a]

Positions of nitro groups	λ, mμ	10^4C_a	Range of n	No. expts.	10^{-3} K, mean value	Rel. st. dev.[b]	10^{-3} K, value adopted
	350	1.0	0.5 to 3.0	7	7.62	2.5	
2,3	*425	1.0	.5 to 8.0	13	7.50	1.5	7.47
	440	1.0	.5 to 8.0	13	7.44	1.7	
	350	0.5	2 to 15	8	3.09	0.8	
2,4		1.0	1 to 20	4			3.14[c]
	*400	0.5	2 to 15	8	3.18	0.6	
		1.0	1 to 20	4			
		0.2	20 to 80	4			
	365	0.4	25 to 75	3	0.411	3.1	
		1.0	5 to 60	8			
		2.0	5 to 62.5	7			
2,5		0.2	20 to 80	4			0.414
	*455	0.4	25 to 75	3	0.414	2.2	
		1.0	5 to 60	8			
		2.0	5 to 62.5	7			
2,6	350	1.0	0.45 to 1.5	11	87.7	4.0	88.0
	*435	1.0	0.45 to 1.5	11	88.4	3.5	
	360	1.0	2.2 to 10.9	7	4.05	2.3	
3,4	380	1.0	1.1 to 19.9	8	4.00	2.2	4.03
	*400	1.0	1.1 to 16.4	10	4.05	2.9	
	*355	1.0	2.5 to 25	10	1.15	1.4	
3,5	365	1.0	2.5 to 25	10	1.21	1.9	1.17
	420	1.0	2.5 to 25	10	1.16	2.8	

[a] The symbols C_a and nC_a signify the molar stoichiometric concentrations of the dinitrophenol and of triethylamine, respectively. Asterisks indicate the wave lengths at which data used in constructing Fig. 1 were obtained. [b] The standard deviation expressed as a percentage of the mean value (see *Anal. Chem.*, **33**, 480 (1961)). [c] R. G. Pearson and D. C. Vogelsong, *J. Am. Chem. Soc.*, **80**, 1038 (1958), obtained the value 2.94 × 10^3 for $K_{\text{assoc.}}$.

Discussion

Comparative Acidities of the Dinitrophenols in Water and Benzene.—In Fig. 2 comparison is made of the relative acidities of the six dinitrophenols in water and benzene, with the inclusion of results obtained previously in this Laboratory for benzoic acid and the phenolic indicator bromophthalein magenta E, and also of results obtained in other laboratories for several phenols in heptane or cyclohexane. Sources of the supplementary data are summarized in Table III.

It is apparent that the acidities of the dinitrophenols in benzene, as measured by association with triethylamine, are not linearly related to the ionic dissociation constants for the dinitrophenols in water. The results obtained in studying association of a large number of *o*-, *m*- and *p*-substituted benzoic acids with diphenylguanidine as the reference base furnished a very satisfactory "norm" of behavior; namely, the linearly related strengths of *meta*-substituted benzoic acids in water and benzene.[1] The available data on phenols are insufficient for establishing a similar norm. However, the plotted points indicate an approximately linear relation, as suggested by the dotted line which passes through the points for 3,5- and 3,4-dinitrophenols. Locating the line in this manner does not, of course, imply that the constants for these two dinitrophenols in water and benzene are accepted as completely accurate and unaffected by structural and environmental factors. It seems reasonable, however, that the reference line should be a little to the left of the bottom group of points, where the aprotic solvent used was heptane or cyclohexane rather than benzene; these are solvents which do not show the tendency which has been observed for benzene and other aromatic solvents to attract phenolic –OH groups, presumably through their π-electron clouds.[13] Even carbon tetrachloride, though the molecule as a whole has zero dipole moment, may associate with phenolic –OH groups because of its Cl^-–C^+ bonds, though to a lesser extent than solvents like benzene.[13a] Such association could compete with the association of phenol with triethylamine and would be consistent with a lower value of log $K_{\text{assoc.}}$ in carbon tetrachloride

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amine association constant being determined was very small. The association constants determined in this work were much larger, and although traces of triethylamine oxide seem likely to have formed during the absorbance measurements, there was no evidence of error from this source.

[13] (a) For example, see studies by L. J. Bellamy and R. L. Williams (*Proc. Roy. Soc.* (*London*), **A254**, 119 (1960)) of solvent effects on the infrared spectra of phenol and hindered phenols. (b) Variable tendencies for phenol to become dimerized in different solvents have also been observed; see F. A. Philbrick, *J. Am. Chem. Soc.*, **56**, 2581 (1934). Analogously, certain carboxylic acids have been found to be more highly dimerized in *n*-heptane than in benzene; H. A. Pohl, M. E. Hobbs and P. M. Gross, *J. Chem. Phys.*, **9**, 408 (1941).

TABLE III

COMPARATIVE STRENGTHS OF SOME ACIDS IN WATER AND IN AN APROTIC SOLVENT[a]

Acid	pK_a, water	Log K for assoc. with Et_3N in an aprotic solvent
Phenol	10.00[b]	1.92,[c] 1.93,[d] 1.75,[e] 1.93[f]
α-Naphthol	9.39[g]	2.08,[c] 2.07,[d] 2.04[f]
Benzoic acid	4.20[h]	3.58[i]
Bromophthalein magenta E (BPM)	4.15[j]	4.44[i]
o-Cresol	10.29[b]	1.84[f]
m-Cresol	10.09[b]	1.84[f]
p-Cresol	10.26[b]	1.81[f]
p-Chlorophenol	9.42[k]	2.30[f]

[a] Data in this Table, together with values for the six dinitrophenols, were used in constructing Fig. 2. (Log K values for the dinitrophenols in benzene are derived from $K_{assoc.}$ values given in Table II. For pK_a values of the dinitrophenols see ref. 2, Table 4.) All pK and log values used are for 25°. $K_{assoc.}$ values are in molar units. [b] A. I. Biggs, *Trans. Faraday Soc.*, **52**, 35 (1956). [c] S. Nagakura and M. Gouterman, *J. Chem. Phys.*, **26**, 881 (1957), from measurements in *n*-heptane by ultraviolet spectrophotometry. [d] A. Julg and M. Bonnet, *Compt. rend.*, **250**, 1839 (1960), from measurements in heptane by ultraviolet spectrography. [e] H. Dunken and H. Fritzsche, *Z. Chem.*, **1**, 127 (1961), through *Chem. Abstracts*, **55**, 19441 (1961), from infrared spectrometric measurements in carbon tetrachloride. The value for log $K_{assoc.}$ at 25° given above was calculated from values (ref. cit.) of ΔH and ΔS. [f] These values apply to association of the phenol with *trimethylamine* in cyclohexane, measured by a partition method; see R. L. Denyer, A. Gilchrist, J. A. Pegg, J. Smith, T. E. Tomlinson and L. E. Sutton, *J. Chem. Soc.*, 3889 (1955). [g] L. K. Creamer, A. Fischer, B. R. Mann, J. Packer, R. B. Richards and J. Vaughan, *J. Org. Chem.*, **26**, 3148 (1961). [h] J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939). [i] See ref. 3d. The systematic name of this phenol is 3′,5′,3″,5″-tetrabromophenolphthalein ethyl ester. [j] See ref. 1, footnote 29. [k] A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

than in heptane (see Table III) and a still lower value (1.65)[14] in benzene.

The dotted reference line conforms to the equation

$$pK_a = -2.35 \log K_{assoc.} + 13.90 \tag{1}$$

$$\text{or } \log K_{assoc.} = -0.426\, pK + 5.91 \tag{2}$$

A rough estimate of the reaction constant ρ for association of phenols with triethylamine in benzene can be obtained by multiplying 0.426 (the negative coefficient of pK in equation 2) by a value of ρ that has been estimated for ionic dissociation of phenols in water (2.23).[15] The value so obtained is $\sim$0.95.

This value of ρ can be combined in the usual way with the experimental values of log $K_{assoc.}$ obtained in the reactions with 3,5-dinitrophenol (3.07) and 3,4-dinitrophenol (3.61) and the rough value estimated above for the reaction with phenol (1.65), to obtain crude values of the substituent constants σ where the substituent is the *meta* or *para* nitro group. The values of σ obtained in this way are 0.75 for *m*-NO_2 and 1.31 for *p*-NO_2. These values are close to the σ values commonly accepted for these groups when substituted in phenols,[16] thus furnishing support for the assumptions made in the preceding discussion.

Assuming for the purpose of further discussion that the dotted line is a reasonably valid expression of the relative intrinsic strengths of phenols in water and benzene, points above this line indicate acidic strengths that are either abnormally high in water or abnormally low in benzene, or both.[17] The reverse is true, of course, for points below the line. Attention was called previously to the discrepancies between observed pK_a values for the six dinitrophenols and the pK values calculated from pK data for phenol and the mono-substituted nitrophenols on the assumption of additive substituent effects—in every case the observed acidity exceeds the calculated acidity.[18] It is noteworthy that the discrepancy is not great and is of approximately equal magnitude in the cases of 3,4- and 3,5-dinitrophenols. One may suspect that 2,4- and 2,5-dinitrophenols are both anomalously strong in water and anomalously weak in benzene, a tendency toward chelation being a factor in the latter solvent.

Location of the point for 2,3-dinitrophenol so near the dotted line is rather surprising, as the difference between the observed and calculated pK values is great.[18] Molecular models show that in this compound the two nitro groups cannot be simultaneously coplanar with the ring.

The difference between the observed and calculated pK values is greatest in the case of 2,6-dinitrophenol.[18] The points for this compound and another di-*ortho*-substituted phenol, bromophthalein magenta E (which is a *para*-substituted derivative of 2,6-dibromophenol), are to the right of the dotted line. Di-*ortho* substituted benzene derivatives show many well known anomalies in behavior, which are usually attributed to a combination of factors, such as steric inhibition of resonance and intramolecular hydrogen bonding. More extensive studies of di-*ortho*-substituted phenols and also benzoic acids are needed.[19]

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[14] This is the value of log $K_{assoc.}$ obtained by interpolation along the dotted line in Fig. 2.

[15] Various values that have been derived for the reaction constant ρ for ionic dissociation of phenols in water at 25° are: (a) 2.01 (L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940); (b) 2.11 (H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953)); (c) 2.30 (R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958)); (d) 2.36 (*ibid.*, **81**, 5343 (1959)); (e) 2.20 (H. van Bekkum, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959)); (f) 2.23 (A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961)). The last value is based on twelve thermodynamic pK values determined in a single laboratory.

[16] For example, compare the respective values 0.71 and 1.27 given in ref. 15b. Calculation of σ for *o*-NO_2 by analogous procedures leads to the following different results (in parentheses) according to the 2-substituted dinitrophenol concerned: 2,3- (1.59); 2,4- (0.64); 2,5- (0.27); 2,6- (1.73). The first and last of these values are reasonable in magnitude; as has been pointed out, the resonance and inductive effects of a substituent can be expected to be approximately the same in the *ortho* and *para* positions; see R. W. Taft, Jr., M. S. Newman and F. H. Verhoek, *J. Am. Chem. Soc.*, **72**, 4511 (1950).

[17] Compare ref. 1, sections 4.2 and 4.3.

[18] See ref. 2. Values of ΔpK ($pK_{exptl.} - pK_{calcd.}$) for the six isomers are as follows (in parentheses): 2,3- (−0.65); 2,4- (−0.25); 2,5- (−0.40); 2,6- (−0.71); 3,4- (−0.13); 3,5- (−0.11). It is also worth noting that the aqueous thermodynamic pK values at 25° of phenol and its mono- and dinitro-derivatives (determined by R. A. Robinson and co-workers) are not linearly related to those of the corresponding benzoic acids (J. F. J. Dippy and co-workers).

[19] Discussion of *ortho* effects in phenols and benzoic acids, with references to other literature, may be found in ref. 1, sections 4.2.d and 4.3.c; also see D. H. McDaniel and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 3756 (1955). A possible steric effect in the association of triethylamine with bromophthalein magenta E in benzene was discussed by M. M. Davis and H. B. Hetzer, *J. Research Natl. Bur. Standards*, **48**, 381 (1952).

Dinitrophenols as Indicators.—In earlier work[3d] the equilibrium constant for association of triethylamine with benzoic acid in benzene was determined indirectly at 25°, using both bromophthalein magenta E and 2,5-dinitrophenol as indicators. By the criterion of association with triethylamine, these two indicators are, respectively about seven times as strong and one-tenth as strong as benzoic acid in this solvent.[20] A third determination of the same association constant was made with the aid of 2,4-dinitrophenol, whose strength (see Table II) more closely matches that of benzoic acid in benzene. From combined absorbance data at 350 and 400 mμ for 22 mixtures the value obtained was 3.64×10^3, with a relative standard deviation of ~5%. A correction was applied as before[3d] for the monomer-dimer equilibrium of benzoic acid, which is the only competing association believed to be of significance in the systems being considered.[21] This belief is strengthened by the close agreement of the three results.

From this and the preceding[1] study, it seems evident that with the aid of suitable indicator acids the relative strengths of acids without visible color can be determined in a broad range of aprotic solvents, not merely in those solvents considered most suitable for infrared measurements (carbon tetrachloride, chloroform) or ultraviolet measurements (heptane, cyclohexane and the like).

Selection of Reference Base.—It is clear that the results of investigations will depend to some extent on the choice of *reference base*. Previous studies have demonstrated characteristic differences in the behavior of primary, secondary and tertiary aliphatic amines in aprotic solvents.[22] The observed differences have helped to clarify solvent effects on basic strengths.[11a] Recently observed differences in the behavior of triethylamine and 1,3-diphenylguanidine as reference bases in benzene suggested an explanation why changing from water to another solvent may cause a reduction in the strengths of carboxylic acids relative to the strengths of phenols.[3d]

The differing effects of water and benzene on the relative strengths of the six isomeric phenols discussed in this paper illustrate the need for further studies of potential *reference acids* for nonaqueous media. Chelation in *o*-nitrophenols can reasonably be considered a factor in the discrepancies observed, and it seems very desirable to seek out new acidic indicators in which a strong tendency toward chelation is absent.[23]

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[20] The strengths of the two indicators are indicated in Tables II and III. The equilibrium constant obtained for association of triethylamine with benzoic acid in benzene was 3.76×10^3 using bromophthalein magenta E as the indicator, and $3.7_2 \times 10^3$ using 2,5-dinitrophenol (see ref. 3d).

[21] Possible associations involving carboxylic acids were considered further in section 4.1 of ref. 1. Phenols seem much less prone than carboxylic acids to dimerize or undergo other kinds of self-association; for example, see ref. 7 and E. N. Lassettre and R. G. Dickinson, *J. Am. Chem. Soc.*, **61**, 54 (1939). Hydrogen bonding between molecules of phenol and carboxylic acid does not seem a likely source of error in the range of concentrations used in this work.

[22] For examples see ref. 11*a*, Table 7 and related discussion, and ref. 3c.

[23] R. P. Bell and R. R. Robinson (*Trans. Faraday Soc.*, **57**, 965 (1961)) observed exceptional behavior of 2,4- and 2,5-dinitrophenols in dioxane–water mixtures, as compared with several carboxylic acids. Chelation may be suspected as a factor here, too.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA]

The Molecular Structure of *n*-Butyl Chloride and *sec*-Butyl Chloride. I. Rigid Framework[1a]

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The molecular structures of gaseous *n*-butyl chloride and *sec*-butyl chloride have been investigated by the sector-microphotometer technique of electron diffraction. A measured molecular parameter represents the average value found for that parameter not only in a particular rotational isomer, but also for all rotational isomers present in the gas phase at room temperature. The average bond lengths, defined in terms of the electron diffraction variable $r_g(0)$ and listed in the order mentioned above were found to be: C–H = 1.110 ± 0.005 Å., 1.110 ± 0.005 Å.; C–C = 1.533 ± 0.003 Å., 1.534 ± 0.003 Å.; and C–Cl = 1.780 ± 0.004 Å., 1.781 ± 0.004 Å. Angles calculated from the $r_g(0)$ internuclear distances were: ∠C–C–C = 112.1 ± 0.9°, 111.4 ± 1.0°; ∠C–C–Cl = 110.8 ± 1.0°, 112.4 ± 1.2°; ∠C–C–H = 110.6 ± 2.0°, 110.6 ± 2.0°. Average root mean square amplitudes of vibration were found to be: C–H = 0.078 ± 0.004 Å., 0.078 ± 0.004 Å.; C–C = 0.055 ± 0.002 Å., 0.056 ± 0.003 Å.; C–Cl = 0.059 ± 0.003 Å., 0.059 ± 0,004 Å. The uncertainties quoted above are estimates of the precision of the measurements involved and are determined from approximate standard errors obtained in the least squares fits of the experimental data and estimates of uncertainties in the measurements involved in determining the value of the scattering variable $q = 40/\lambda \sin \theta$. These uncertainties do not reflect possible sources of error in the kinematic scattering theory employed.

The structures of the two molecules reported here are part of a larger study, which it is hoped will encompass as many of the butyl halides as possible. This series of molecules has long been used by physical organic chemists to correlate reaction rates with steric hindrance and various electronic effects.[2] It will be the main purpose of this work to look for these same environmental influences on the ground state structures of the molecules studied. The conclusions drawn from the pre-

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[2] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959.