

of the recombination with H_2 as the third body takes place by this mechanism we find that σ_2 lies between 3.6 and 5.5×10^{-8} cm. Since the recombination probably takes place by both this mechanism and Steiner's the true value of the diameter σ_2 is somewhat smaller.

On the other hand, if we assume σ_2 to be equal to Steiner's σ_{AM} , which is not unreasonable, we find that our mechanism will go at a rate three to six times the rate of Steiner's mechanism.

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A STUDY OF MOLECULAR ORGANIC COMPOUNDS. IV.¹ THE MOLECULAR ORGANIC COMPOUNDS OF PHENOL, THEIR PARACHORS AND REFRACTIVITIES²

BY C. A. BUEHLER, J. H. WOOD, D. C. HULL AND E. C. ERWIN

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The molecular organic compounds of phenol, as a group, represent one of the simplest types. These compounds, although possessing fairly sharp melting points, decompose so readily into the original components that attempts to gain any information as to their structure by chemical methods have been unsuccessful. In the present investigation two physical methods have been applied to the study of the structure of some of these molecular compounds.

In Table I are listed the compounds which have been isolated and studied. Most of these have only previously been shown to exist by their freezing point curves. Worthy of note are the great number of them, the usual molecular ratios of 1:1 and 2:1 and the fact that the second components all contain amino groups.

The parachors as determined, both for some of the components and their molecular compounds, by the formula of Sugden³ are given in Tables II and III. Among the components it is to be noted that the observed parachors are lower than the calculated values and with increasing temperature a steady rise occurs much in the same way as with the alcohols and fatty acids.⁴ The same relation exists among the molecular compounds although the temperature coefficients and the differences between

¹ Contribution III, *THIS JOURNAL*, **53**, 4094 (1931).

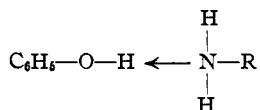
² Parts of this paper are taken from the Masters' Theses presented by David C. Hull and E. C. Erwin at the University of Tennessee.

³ Sugden, "The Parachor and Valency," George Routledge and Sons, Ltd., London, 1930, p. 30.

⁴ Sugden, Ref. 3, p. 167.

the observed and calculated values are greater here. It is likely that we are dealing in both cases with association, the amount of which becomes less and less with an increase in temperature.

It is not possible, at present, by any known method to find the degree of association at any one temperature. However, the differences between the observed and calculated values of the parachors for the molecular compounds, with decreasing temperature, do approach a maximum negative value. According to Sugden⁵ such a negative value is due to a bond consisting either of a pair of electrons (the semi-polar double bond) or of a single electron. Although the latter is used freely by Sugden⁵ it finds less favor in other quarters.⁶ We are discarding it as a possibility since the stability of the compounds concerned does not seem to be of a sufficiently low order to warrant such a type of union. There remains the semipolar double bond which (excluding ring formation, which does not seem likely due to the fact that an unstable four-membered ring would result) may account for the type of formula recently advanced:⁷



From Sidgwick's⁸ work among the ortho substituted phenols it appears that the semipolar bond above has the usual value of -1.6 plus a value of -12.8 due to the rise in covalency of the hydrogen from 1 to 2. The total value, -14.4 , as Table III shows, may in general be considered as the maximum for the differences between the observed and calculated parachors and the formula above may, therefore, be considered as the most probable for the molecular compounds of phenol.

The refractive indices for the components and their molecular compounds are shown in Table IV and the molecular refractions as obtained by the Lorenz and Lorentz formula are given in Table V. A comparison of the observed and calculated molecular refractions at 20° shows in general, in the case of the components, some optical exaltation, while with the molecular compounds optical depression is usually exhibited. In either case the optical exaltation for any amine is greater than that for the molecular compound which it forms with phenol. Although this reduction in refraction was originally attributed⁹ to an increase in the valence of the nitrogen of the amine it may be considered, by the more modern interpreta-

⁵ Sugden, Ref. 3, p. 131.

⁶ Sidgwick and Bayliss, *J. Chem. Soc.*, 2033 (1930); Pauling, *THIS JOURNAL*, **53**, 3229 (1931).

⁷ Buehler, Alexander and Stratton, *ibid.*, **53**, 4094 (1931).

⁸ Sidgwick and Bayliss, Ref. 6, p. 2032.

⁹ Eisenlohr, *Ber.*, **44**, 3188 (1911).

tion of Smyth,¹⁰ as being due to the attachment of the hydrogen of the phenol to the nitrogen of the amine as proposed in the formula above. In Table V these differences are shown in the last column, which is really a comparison of the differences between the observed and calculated molecular refractions of the molecular compounds with the sum of the like differences of the two components.¹¹ It is obvious that if the mixture law were true these values would all be zero. Since they are all negative in value they may be interpreted in terms of a union between the two molecules. The differences, which are approaching zero with increasing temperature, are small doubtless due (1) to the partial dissociation of the molecular complex and (2) as Smyth has suggested to the counterbalancing effect produced by the weakening of the forces which the hydrogen exerts on the oxygen of the phenol.

Experimental Part

The preparation, purification and analysis of the molecular compounds were accomplished in the main from the second components and by the methods already described. In doubtful cases freezing point curves were constructed.

Purification of Components.—The components concerned either as individuals or otherwise in the parachor and refractivity determinations were specially purified as stated below.

Phenol.—Method of Sidgwick and Bayliss;¹² m. p. (corr.) 40.5°.

Aniline.—The commercial product, distilled twice, was converted into acetanilide which was crystallized three times from water containing a little acetic acid. This solid was hydrolyzed, the aniline obtained being treated with acetone to remove thiophene by the method of Hantzsch and Freese.¹³ The amine was finally recovered from the hydrochloride by treatment with sodium carbonate solution and, after being dried over solid potassium hydroxide and fractionally distilled twice, it boiled at 184.3° (corr.).

***o*- and *m*-Toluidines.**—In general, by the method of Berliner and May;¹⁴ b. p.'s *o*- 199.3° (corr.), *m*- 203.0° (corr.).

***p*-Toluidine.**—In general, by the method of Gans and Harkins;¹⁵ m. p. 43.4° (corr.).

4-Amino-1,3-dimethylbenzene.—The c. p. product, first distilled, was converted into the hydrochloride, which was fractionally crystallized twice from absolute alcohol

¹⁰ Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, 1931, p. 160.

¹¹ This method of comparison seemed advisable because of the unreliability of the atomic refractions at temperatures above 20° as well as that of nitrogen at 20°. This latter value varies so much even among aromatic primary amines that the mean loses much of its significance. In contrast to the parachor discussion the differences between the observed and calculated values of the components are attributed to the difficulty with the atomic refractions and not to association.

¹² Sidgwick and Bayliss, Ref. 6, p. 2027.

¹³ Hantzsch and Freese, *Ber.*, 27, 2966 (1894).

¹⁴ Berliner and May, *THIS JOURNAL*, 49, 1008 (1927).

¹⁵ Gans and Harkins, *ibid.*, 52, 2292 (1930).

and then twice from water. The product thus obtained was treated with sodium carbonate solution to free the xyldine which was dried over solid potassium hydroxide and then fractionally distilled twice under reduced pressure; b. p. 214.3° (corr.).

Physical Measurements.—Surface tensions were determined by the maximum bubble pressure method of Sugden.¹⁶ The bubbler was immersed in a constant temperature bath and readings of the manometer level were made with a cathetometer. Highly purified benzene was used in the determination of the diameter of the larger bubbler tube after the diameter of the smaller one had been measured by a filar micrometer.

Densities of the liquids were determined with an ordinary 10-cc. pycnometer; the densities of the vapors at the temperatures employed were negligible and were, therefore, undetermined.

The refractivity measurements at 45, 60 and 80° were made by a Pulfrich refractometer.

TABLE I
MOLECULAR COMPOUNDS OF PHENOL

Second component	M. p., °C. (corr.)	F. p., °C. (litr.)	Color	Mol. ratio	Calcd.	N. % Found	Found
Aniline	32.6	32 ^a	Colorless	1:1	7.48	7.64	7.53
<i>o</i> -Toluidine	35.6	34 ^b	White	1:1	6.96	6.93	6.78
<i>m</i> -Toluidine	-7 ^c	...	Colorless	1:1	6.96	6.78	6.78
<i>p</i> -Toluidine	33.0	28.5 ^d	Colorless	1:1	6.96	6.97	6.88
4-Amino-1,3-dimethyl- benzene	16 ^e	16 ^b	White	1:1	6.51	6.37	6.41
α -Naphthylamine	29.1	28.8 ^d	Purple	1:1	5.90	5.70	5.96
β -Naphthylamine	84.4	83.5 ^b	White	1:1	5.90	5.96	5.70
Benzidine	128.4	...	Light gray	1:1	10.07	10.25	10.27
<i>o</i> -Phenylenediamine	44.2	43.5 ^e	Brown	1:1	13.85	13.98	14.08
<i>o</i> -Phenylenediamine	29.7	29.5 ^e	Colorless	4:1	5.78	5.63	5.67
<i>m</i> -Phenylenediamine	58.0	52.6 ^e	Gray	3:2	11.23	11.09	11.11
<i>p</i> -Phenylenediamine	98.6	...	Reddish- brown	1:1	13.85	13.87	13.91
<i>p</i> -Phenylenediamine	106.5	105 ^e	Dark brown	2:1	9.45	9.61	9.38
Urea	61.5	60.4 ^d	White	2:1	10.07	10.09	10.22
Acetamide	42.9	40.8 ^f	White	2:1	5.66	5.59	5.69
Acetamide-water	42.1	...	Pink	2:1:1	5.28	5.26	5.17
Benzamide	31.0 ^g	23.5 ^f	White	2:1	4.53	4.48	4.62
Diethylamine	12 ^g	...	Pink	1:1	8.37	8.27	8.23
Pyridine	-19 ^g	-10 ^g	White	1:1	54.39 ^h	54.46	54.40
Pyridine	4 ^g	5 ^g	White	2:1	70.41 ^h	70.62	70.38

^a Melting point of the compound first obtained by Hübner, *Ann.*, 210, 342 (1881).

^b Kremann, *Monatsh.*, 27, 91 (1906).

^c Freezing point, $\pm 1^\circ$ accuracy.

^d Philip, *J. Chem. Soc.*, 83, 814 (1903).

^e Kremann and Petritschek, *Monatsh.*, 38, 405 (1917).

^f Kremann and Wenzig, *ibid.*, 38, 479 (1917).

^g Bramley, *J. Chem. Soc.*, 109, 474 (1916).

^h Percentage of phenol; determined by titration of tribromophenol with alkali.

¹⁶ Sugden, Ref. 3, p. 208.

Table II
 DENSITIES, SURFACE TENSIONS AND PARACHORS OF COMPONENTS

Compounds	Temp., °C.	d	γ	P (obs.)	P (calcd.)	$\frac{P \text{ (obs.)} - P \text{ (calcd.)}}$
Phenol	50	1.0499	37.74	222.0 ¹⁷	227.1	-5.1
	70	1.0328	35.45	222.2		-4.9
	90	1.0150	33.35	222.7		-4.4
	120	0.9885	30.18	223.0		-4.1
	150	.9588	26.77	223.1		-4.0
Aniline	50	.9957	40.10	235.2	236.7	-1.5
	70	.9780	37.63	235.7		-1.0
	90	.9602	35.22	236.1		-0.6
	120	.9338	31.60	236.3		-0.4
	150	.9052	28.07	236.6		-0.1
<i>o</i> -Toluidine	50	.9743	37.49	272.0	275.7	-3.7
	70	.9575	35.18	272.4		-3.3
	90	.9405	32.92	272.7		-3.0
	120	.9152	29.70	273.1		-2.6
	150	.8890	26.52	273.3		-2.4
<i>m</i> -Toluidine	25	.9851	37.73	269.4	275.7	-6.3
	50	.9653	35.62	271.0		-4.7
	70	.9490	33.40	271.3		-4.4
	90	.9331	31.59	272.1		-3.6
	120	.9068	28.61	273.1		-2.6
<i>p</i> -Toluidine	50	.9619	34.88	270.5	275.7	-5.2
	70	.9444	32.80	271.3		-4.4
	90	.9276	30.89	272.2		-3.5
	120	.9020	28.16	273.5		-2.2
	4-Amino-1,3-dimethylbenzene	25	.9723	36.75	307.2	314.7
50		.9520	34.46	308.2		-6.5
70		.9355	32.38	308.8		-5.9
90		.9197	30.39	309.1		-5.6
120		.8950	27.31	309.3		-5.4
150		.8695	24.45	309.7		-5.0

 TABLE III
 DENSITIES, SURFACE TENSIONS AND PARACHORS OF MOLECULAR COMPOUNDS

Compounds	Temp., °C.	d	γ	P (obs.)	P (calcd.) ^a	$\frac{P \text{ (obs.)} - P \text{ (calcd.)}}$
Phenol-aniline	50	1.0289	39.17	454.9	463.8	- 8.9
	70	1.0112	36.99	456.3		- 7.5
	90	0.9932	34.90	457.9		- 5.9
	120	.9658	31.42	458.7		- 5.1
	150	.9366	27.96	459.4		- 4.4
Phenol- <i>o</i> -toluidine	50	1.0153	38.12	492.2	502.8	-10.6
	70	0.9976	35.82	493.2		- 9.6
	90	.9794	33.53	494.2		- 8.6
	120	.9522	30.16	495.0		- 7.8
	150	.9240	26.84	495.5		- 7.3

¹⁷ Sidgwick and Bayliss' values, Ref. 6, p. 2031, vary from 222.3 at 49.6° to 224.8 at 147.5°.

TABLE III (Concluded)

Compounds	Temp., °C.	d	γ	P (obs.)	P (calcd.) ^a	$\frac{P \text{ (obs.)} - P \text{ (calcd.)}}$
Phenol- <i>m</i> -toluidine	25	1.0292	38.93	488.1	502.8	-14.7
	50	1.0090	36.67	490.6		-12.2
	70	0.9918	34.49	491.5		-11.3
	90	.9748	32.71	493.4		- 9.4
	120	.9485	29.74	495.2		- 7.6
	150	.9204	26.72	496.8		- 6.0
Phenol- <i>p</i> -toluidine	50	1.0084	36.18	489.1	502.8	-13.7
	70	0.9911	34.11	490.5		-12.3
	90	.9733	32.18	492.2		-10.6
	120	.9468	29.29	494.4		- 8.4
Phenol-4-amino-1,3-dimethylbenzene	25	1.0190	38.15	524.7	541.8	-17.1
	50	0.9997	35.76	526.3		-15.5
	70	.9826	33.65	527.4		-14.4
	90	.9654	31.67	528.7		-13.1
	120	.9391	28.73	530.4		-11.4
	150	.9115	25.97	532.8		- 9.0

^a P (calcd.) = sum of P 's (calcd.) of components.

TABLE IV
REFRACTIVE INDICES AT 45°

Compound	$\frac{dn}{dt} \times 10^4$ ^a	n_D^{45}	n_α^{45}	n_β^{45}
Phenol	47	1.54018	1.53498	1.55382
Aniline	53	1.57285	1.56646	1.59052
<i>o</i> -Toluidine	51	1.56020	1.55377	1.57610
<i>m</i> -Toluidine	49	1.55609	1.54992	1.57210
<i>p</i> -Toluidine	49	1.55397	1.54778	1.56950
4-Amino-1,3-dimethylbenzene	48	1.54729	1.54156	1.56242
Phenol-aniline	48	1.55742	1.55145	1.57270
Phenol- <i>o</i> -toluidine	48	1.55300	1.54725	1.56780
Phenol- <i>m</i> -toluidine	48	1.55036	1.54466	1.56506
Phenol- <i>p</i> -toluidine	47	1.54992	1.54422	1.56464
Phenol-4-amino-1,3-dimethylbenzene	48	1.54747	1.54192	1.56184

^a Mean of the temperature coefficients of the D , H_α and H_β lines.

TABLE V

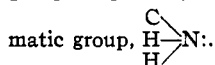
VARIATION OF MOLECULAR REFRACTION WITH TEMPERATURE
Observed values at 20° calculated by use of the two temperature coefficients

Temp., °C.	MR_D (obs.)	EMR_D ^a	Temp., °C.	MR_D (obs.)	EMR_D ^a	$\frac{EMR_D \text{ (M. C.)} - EMR_D \text{ (C's)}^b}$
	Phenol			Phenol-aniline		
20	27.91	0.09	20	58.07	-0.38	-0.40
45	28.00	.17	45	58.27	- .18	- .39
60	28.06	.23	60	58.47	.02	- .31
80	28.11	.28	80	58.63	.18	- .27

TABLE V (Concluded)

Temp., °C.	MR_D (obs.)	EMR_D^a	Temp., °C.	MR_D (obs.)	EMR_D^a	EMR_D (M. C.) - EMR_D (C's) ^b	
	Aniline			Phenol- <i>o</i> -toluidine			
20	30.55	-.07	20	62.83	-.24	-.37	
45	30.66	.04	45	63.11	.04	-.28	
60	30.72	.10	60	63.29	.22	-.21	
80	30.79	.17	80	63.45	.38	-.20	
	<i>o</i> -Toluidine			Phenol- <i>m</i> -toluidine			
20	35.28	.04	20	63.03	-.04	-.27	
45	35.39	.15	45	63.26	.19	-.25	
60	35.44	.20	60	63.44	.37	-.21	
80	35.54	.30	80	63.59	.52	-.18	
	<i>m</i> -Toluidine			Phenol- <i>p</i> -toluidine			
20	35.38	.14	20	63.00	-.07	-.30	
45	35.51	.27	45	63.26	.19	-.26	
60	35.59	.35	60	63.44	.37	-.21	
80	35.66	.42	80	63.59	.52	-.23	
	<i>p</i> -Toluidine			Phenol-4-amino-1,3-dimethylbenzene			
20	35.38	.14	20	67.76	.07	-.21	
45	35.52	.28	45	68.00	.31	-.19	
60	35.59	.35	60	68.19	.50	-.13	
80	35.71	.47	80	68.36	.67	-.12	
	4-Amino-1,3-dimethylbenzene						
20	40.05	.19					
45	40.19	.33					
60	40.26	.40					
80	40.37	.51					

^a $EMR_D = MR_D$ (obs.) - MR_D^{20} (calcd.). The atomic refractions used are the revised values of Eisenlohr, *Z. physik. Chem.*, 75, 605 (1911); 79, 134 (1912). Similar calculated molecular refractions may be obtained by the refractions of the electron groups as given by Smyth, Ref. 10, p. 152. In the latter case 6.02 is used for the aromatic group,



^b EMR_D (M. C.) - EMR_D (C's) is the difference between the observed and calculated molecular refractions of the molecular compounds minus the sum of the like differences for the components.

Summary

New molecular compounds of phenol have been isolated.

The densities, surface tensions and refractivities of certain of these compounds over a range of temperature have been determined.

The parachors and molecular refractions both increase with increase in temperature.

A comparison between the observed and calculated values for the parachors and molecular refractions indicates that the bond between the components in the molecular compounds has a negative value.

An electronic formula, based upon these determinations, has been proposed.

KNOXVILLE, TENNESSEE

[CONTRIBUTION FROM EAST LONDON COLLEGE, UNIVERSITY OF LONDON]

THE PINACOL-PINACOLONE REARRANGEMENT. THE EXAMINATION OF SOME ORTHO-SUBSTITUTED BENZOPINACOLS

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It is generally recognized that the values for the relative migratory powers of aromatic hydrocarbon radicals in the pinacol-pinacolone rearrangement are least liable to error when they are obtained from studies of the rearrangement of tetraarylpinacols, for the reason that in such cases there is the least possibility of the end products of the reaction arising in any other way than by a direct pinacol-pinacolone change. In this connection *o*-substituted benzopinacols have been but little examined; of the simple compounds of this class only *sym*.-2,2'-dichlorobenzopinacol and *sym*.-2,2'-dibromobenzopinacol have been at all fully investigated.¹ These pinacols rearranged slowly and the resulting pinacolones were very resistant to attack by alcoholic potash so that a complete decomposition thereby into the corresponding triarylmethanes and aromatic acids was not effected, but it was concluded that in the rearrangements only the unsubstituted phenyl group underwent migration.

Recently Bailar² stated that *sym*.-2,2'-dimethylbenzopinacol and *sym*.-2,2'-dimethoxybenzopinacol could not be rearranged either by iodine and acetic acid, or by acetyl chloride and acetic acid, prolonged treatment with the latter reagent giving rise to unidentifiable oils. He considered these results to be in good agreement with the theoretical conclusions of Lagrave.³ Bailar overlooked the fact that the rearrangement of *sym*.-2,2'-dimethylbenzopinacol had already been described⁴ and that of the phenyl and *o*-tolyl groups the former had been shown to migrate the more readily.⁵

We therefore decided to repeat the rearrangement of *sym*.-2,2'-dimethylbenzopinacol (I), determining the relative migratory powers of the phenyl

¹ Koopal, *Rec. trav. chim.*, **34**, 115 (1915).

² Bailar, *THIS JOURNAL*, **52**, 3596 (1930).

³ Lagrave, *Ann. chim.*, **10**, VIII, 363 (1927).

⁴ Hatt, *J. Chem. Soc.*, 1623 (1929).

⁵ Of the ten pinacols described by Bailar as new, two were already known: *sym*.-2,2'-dimethylbenzopinacol [W. D. Cohen, *Rec. trav. chim.*, **38**, 123 (1919); Boyd and Hatt, *J. Chem. Soc.*, 898 (1927)] and *sym*.-2,2'-dimethoxybenzopinacol [Cohen, *Rec. trav. chim.*, **38**, 123 (1919), and **39**, 258 (1920)].