[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

AN OBSERVATION ON THE RELATION BETWEEN THE MELTING POINTS OF THE DISUBSTITUTED ISOMERS OF BENZENE AND THEIR CHEMICAL CONSTITUTION

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In an investigation of the melting points of the disubstituted derivatives of benzene, it was noticed that a definite relationship does exist between the melting point of the isomers and their chemical constitution.

The derivatives were placed in one of two classes on the basis of their structure. Class A, in which the disubstituted derivative contains *one* ortho-para orienting group (1, 2, 6); and *one* meta orienting group (1, 2, 6); and Class B, in which the disubstituted derivative contains *two* ortho-para orienting or *two* meta orienting groups.

Division of Groups. The substituent groups were divided into two classes, those that are meta orienting and those that are ortho-para orienting in character. Table I lists the various groups according to these properties.

The Order of the Melting Points for the Disubstituted Derivatives of Benzene. The following rules are postulated from the data collected on the melting points of the disubstituted derivatives of benzene:

Rule I. When the disubstituted benzene derivative contains *one* meta orienting group and *one* ortho-para orienting group, the order of the melting points for the isomers is: ortho < meta < para.

Rule II. When the disubstituted benzene derivative contains *only* ortho-para orienting or *only* meta orienting groups, the order of the melting points for the isomers is: meta < ortho < para.

In Table II are listed the melting points of various disubstituted derivatives of benzene containing *one* ortho-para orienting group and *one* meta orienting group. It is seen by inspection that Rule I holds.

In Table III are recorded the melting points of the various disubstituted derivatives of benzene containing *only* ortho-para orienting groups or *only* meta orienting groups. The order of the melting points for these isomers follows Rule II, namely $m < o < p$.

DISCUSSION

At the present time no satisfactory explanation to account for Rules I and II is evident.

In view of the complex interplay of factors affecting the absolute values of melting points, it was anticipated that some exceptions to the postulated rules would exist.

It is well known that the melting points of organic compounds are not readily predicted. This paper allows one to predict with reasonable accuracy the order of the melting points of the isomers of the disubstituted derivatives of benzene and should be of value in both applied and theoretical organic chemistry.

TABLE I

DIVISION OF GROUPS

META ORIENTING GROUPS	ORTHO-PARA ORIENTING GROUPS
$-NO_2$	$-N(CH_3)_2$
$-C\equiv N$	$-N(COCH_3)_2$
$-C(=O)-CH_3$	$-NH_2$
$-C(=O)-H$	$-OH$
$-C(=O)-OH$	$-O-CH_3$
$-N=O$	$-O-C_2H_5$
$-C(=O)-OCH_3$	$-F$
$-C(=O)-NH_2$	$-Cl$
$-SO_3H$	$-Br$
$-C(=O)-Cl$	$-I$
	$-CH_3$
	$-C_2H_5$
	$-NHCOCH_3$
	$-O-C(=O)-CH_3$
	$-C_6H_5$
	$-CH_2COOH$
	$-CH=CHCOOH$
	$-N=NC_6H_5$
	$-CH_2CN$
	$-CH_2Cl$
	$-CH_2Br$
	$-CHCl_2$

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TABLE II

Melting Points for Rule I Disubstituted Derivatives of Benzene

Disubstituted derivative	Melting point of isomer, °C (3, 4, 5)		
	Ortho	Meta	Para
(a) Amino derivatives			
aminobenzamide	108	113–114	182.9
aminobenzoic acid	144–145	173–174	187–188
aminobenzonitrile	51	53	86
(b) Hydroxy derivatives			
hydroxybenzaldehyde	−7	106	116–117
hydroxybenzoic acid	159	201	214.5
(c) Halogen derivatives			
chlorobenzaldehyde	11	17–18	47.8
iodobenzaldehyde	37	57	77
fluorobenzamide	116	130	154.5
iodobenzamide	183.6	186.5	217.6
fluorobenzoic acid	120–122	124	182–184
chlorobenzoic acid	141–142	158	242–243
bromobenzoic acid	148	154	251
iodobenzoic acid	−28.5	162	187.5
fluoronitrobenzene	−5.9	1.7	26.5
chloronitrobenzene	32.5	44.4	83.5
bromonitrobenzene	43	56	127
(d) Methoxy and ethoxy derivatives			
ethoxybenzoic acid	19–20	135–137	195
methoxybenzoic acid	98	107–108	184.2
(e) Nitro derivatives			
nitroacetanilide	93	155	215
nitroaniline	71.5	114	146–147
nitroanisole	9.4	38	54
nitrobenzyl bromide	46–47	58	100
nitrophenatole	5–6	34	59–60
nitrodiphenyl	37	61	113–114
nitrophenol	44–45	96–7	113–114
nitrotoluene	α,−10.6 β, −4.1	15.5	51.3
(f) Toluene derivatives			
toluic acid	104–105	110–111	179–180
(g) Miscellaneous derivatives			
acetamidobenzoic acid	184–186	249	252
phenylbenzoic acid	113–114	160–161	219–220
(h) Exceptions			
bromobenzamide	156	150	190
bromobenzonitrile	51	38	113
chlorobenzamide	141	134.5	178.3
ethylbenzoic acid	67	47	112–113
hydroxyacetanilide	203	149	168
hydroxybenzamide	140	170.5	162
iodo-nitrobenzene	49.4	36	171.5
toluamide	147	97	165
tolunitrile	−13	−23	29.5
nitrobenzyl chloride	48–49	45–47	71
nitrobenzyl cyanide	84	61–62	116–117
nitrocinnamic acid	243–245	200–201	286–288
nitrosotoluene	72.5	53.5	48.5

TABLE III

MELTING POINTS FOR RULE II DISUBSTITUTED DERIVATIVES OF BENZENE

DISUBSTITUTED DERIVATIVE	MELTING POINT OF ISOMER, °C (3, 4, 5)		
	Meta	Ortho	Para
(a) Two meta orienting groups			
sulfobenzoic acid	98	105	260
dinitrobenzene	89.8	117	173
nitrobenzamide	142–143	176.6	200–201
nitrobenzoic acid	140–141	147.5	240–242
(b) Two ortho-para orienting groups			
aminodiphenyl	30	45–46	50–52
aminophenol	122	173	184–186
anisidine	<−12	5.2	59
aminoacetanilide	70	132	161–162
acetylanisidine	80	87–88	137–138
acetotoluide	65.5	110	153
bromoacetanilide	87.5	99	168
aminoazobenzene	57	123	126
chloroacetanilide	72.5	88	178.4
diaminobenzene	62.8	103	140
diethoxybenzene	12.4	43–45	71–72
dimethylbenzene	−47.4	−25	13.2
dimethoxybenzene	−52	22.5	56
ethylaniline	−64	−43	−5
hydroxyphenylacetic acid	129	145–147	148
methoxyphenol	<−17.5	28.3	53
methylacetanilide	65.5	110.4	146–147
xylylene cyanide	28–29	59–60	98
toluidine	−31.5	α, −24.4 β, −16.3	43.7
xylenedibromide	77	94.5	144
xylenedichloride	34.2	55	100.5
(c) Dihalo benzenes			
dibromobenzene	−6.9	1.8	87.8
dichlorobenzene	−24.8	−17.6	53
(d) Halo anilines			
fluoroaniline	—	−34.6	−1.9
chloroaniline	−10.4	0.0	71
bromoaniline	18.5	31.5	66.4
iodoaniline	27	56.5	62
(e) Halo phenols			
fluorophenol	13.8	16.1	28.5
iodophenol	40	40.4	94
(f) Halo toluenes			
fluorotoluene	−110.8	<−80	—
chlorotoluene	−47.8	−34	7.5
bromotoluene	−39.8	−28	28.5
(g) Miscellaneous derivatives			
chlorobromobenzene	−21.2	−12.6	67.4
bromoiodobenzene	−9.3	−2.1	92

TABLE III—*Concluded*

DISUBSTITUTED DERIVATIVE	MELTING POINT OF ISOMER, °C (3, 4, 5)		
	Meta	Ortho	Para
(h) Exceptions			
azophenol	205	172	216
aldehydobenzoic acid	164–166	97–98	285
acetyltoluidide	303	296	306–307
hydroxyactanilide	149	203	168
acetylbenzoic acid	172	114–115	200
aminocinnamic acid	181–182	158–159	175–176
dihydroxybenzene	110	105	170
hydroxyazobenzene	114–116	82.5	155–156
nitrobenzaldehyde	58	40.9	106
methylnitrobenzoate	78.5	−8	96
ethylphenol	−4	<−18	46–47
nitrobenzonitrile	117–118	109–110	147–149
phthalic acid	347	231	sub. >300
hydroxydiphenyl	75–78	56–57	164–165
dimethylphthalate	67–68	0.0	140
chlorophenol	29	α, 7	
		β, 0.0	41
		γ, −4	
terphenyl	85	50	215
phthalic aldehyde	89–90	56	115–116

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