Tetrahedron. 1964, Vol. 20, pp. 841 to 853. Pergamon Press Ltd. Printed in Northern Ireland

MESOMERIC AND ELECTROMERIC FACTORS IN THE MONONITRONAPHTHYLAMINES

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(*Received* 6 *December* 1963)

Abstract—The electric dipole moments of the ten mononitronaphthylamines with the substituents in non-adjacent positions and the 1-nitronaphthalene and 1-naphthylamine have now been completed in the solvents—benzene and dioxan. Interaction moments have been calculated for the mononitronaphthylamines in each solvent and linear relationship with these and the corresponding σ values ensue for the following substituent positions (i) homonuclear (ii) heteronuclear in quinonoid positions (iii) heteronuclear in non-quinonoid positions. The homonuclear isomers exhibit similar features to the *m*- and *p*-nitroanilines. The isomers of type (ii) provide direct evidence for the existence of quinonoid resonance forms and in two cases at least their increased contribution in dioxan as opposed to benzene solution. In particular, 5-nitro-1-naphthylamine appears to have a negligible quinonoid contribution in benzene but quite appreciable in dioxan. Thus, the behaviour brings out the electromeric nature of the solute molecule by intermolecular hydrogen bonding with the solvent. This effect appears to be significant only when the substituents are in quinonoid positions. Apart from substituents in such positions and small deviations, the isomers obey the relationship obtained by Smith and Walshaw[1] for various *m*- and *p*-substituted anilines.

INTRODUCTION

CONSIDERABLE work has been carried out in order to determine the effects of substituents in benzene compounds. These effects are usually expressed in terms of Hammett σ constants[2] or modifications thereof (e.g. σ_I and σ_R)[3] where σ is a constant which takes into account the inductive and mesomeric interactions between the substituent and the remainder of the molecule, in so far as it affects the electron density at the reaction centre, but excludes mutual conjugation. The naphthalene series affords a logical extension to such investigations into substituent effects in aromatic systems and a few series of reaction rate data for substituted naphthalenes are now available.[4–6] In addition, Dewar and Grisdale[7] from theory and certain assumptions have calculated σ values for disubstituted naphthalenes.

The influence of substituents is not limited to detection by parameters derived from reaction rate data. It would be expected that any property which enables the effect of a substituent on the electron density in another part of the molecule to be determined should also be useful in the quantitative estimation of substituent effects. In fact, it is found that substituent constants closely parallel sets of physical data which are related to the electron density at a particular part of the molecule. For instance,

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Rao[8] has reported a correlation of the UV absorption spectra of substituted benzenes with their reactivities, and Whetsel *et al.*[9] have shown that a linear relationship exists between the symmetric and asymmetric stretching frequencies of the amino group in various substituted anilines and the σ values for these substituents. Relationships between electric dipole moments and σ constants for several substituted benzene compounds have also been reported by van Beek[10] and by Rao *et al.*[11]

Pearson[12] has examined the electronic spectra of the nitronaphthylamines in polar and non-polar solvents and has attempted to correlate the magnitude of the bathochromic shift—on changing from a non-polar to a polar solvent—with mesomeric interaction.

Some dipole moment work has been carried out previously on some of the nitronaphthylamines in both benzene and dioxan solution[13,14] (Table 3). However, only two of these isomers have been examined in dioxan.

It was considered that dipole moment data could be better utilized for obtaining information about substituent effects by calculating the additional moment (μ_{int}) arising from the interaction between the substituent groups; i.e. $\mu_{\text{int}} = \mu_{\text{obs}} - \mu_{\text{calc}}$, where μ_{obs} is the measured dipole moment and μ_{calc} is that obtained by vector addition of the individual group moments assuming no interaction occurs between the two substituents. A modified vectorial μ_{int} has been used here (see later).

It is well known that the dipole moments of aromatic amines, and consequently the μ_{int} values, are increased in solvents capable of forming intermolecular hydrogen bonds with the amino hydrogen atoms.[1] Hammett σ constants, on the other hand, are taken to be independent of the solvent. This factor is accounted for by the value of the reaction constant ρ in the Hammett equation where ρ is related to the electron density at the reaction centre. Thus, a good correlation would not be expected between σ constants and μ_{int} values unless the solvent effect is constant throughout the series under consideration. It was therefore decided to measure the dipole moments of the isomeric mononitronaphthylamines in benzene and dioxan solutions so that any relationships between the μ_{int} values and the σ constants, derived for the nitro substituents from the pK_a values of these aromatic amines in water at 25°, could be examined and any differences caused by solvent effects could be observed.

In addition it was hoped that the dipole moment data would (i) give a better insight into any mesomeric interaction when the substituents were in different rings (ii) detect conjugation between the groups across the resonant system (iii) yield evidence for the electromeric effect as a result of intermolecular hydrogen bonding of the hydrogen in the amino group to an oxygen in dioxan.

Dipole moments

At least five solutions varying in weight fraction between 0·001–0·01 were used in the determination of each dipole moment. Solute-solute interactions have been

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assumed to be negligible over this range of concentration and in all cases the plots of the dielectric constants ε_{12}, specific volumes v_{12} and squares of the refractive indices n_{12}^2 against their weight fractions w_2 showed no deviation from linearity. The equations employed were:

$$\varepsilon_{12} = \varepsilon_1 + \alpha w_2,\ v_{12} = v_1 + \beta w_2, \quad \text{and} \quad n_{12}^2 = n_1^2 + \gamma w_2 \qquad (1)$$

where α, β and γ are calculated from the quotients shown below in order to avoid giving undue weight to the results in the most dilute solutions:

$$\Sigma(\varepsilon_{12} - \varepsilon_1)/\Sigma w_2 = \alpha,\ \Sigma(v_{12} - v_1)/\Sigma w_2 = \beta \quad \text{and} \quad \Sigma(n_{12}^2 - n_1^2)/\Sigma w_2 = \gamma \qquad (2)$$

The molar polarization at infinite dilution $P_{2\infty}$ was calculated from the equation,

$$P_{2\infty} = M_2[3\alpha v_1/(\varepsilon_1 + 2)^2 + (\varepsilon_1 - 1)(v_1 + \beta)/(\varepsilon_1 + 2)] \qquad (3)$$

taking ε_1 as 2·2725 and v_1 as 1·14445, and the dipole moment μ was obtained from the usual relationship:

$$\mu = 0{\cdot}01281\ (P_0 T)^{1/2}\text{D} \qquad (4)$$

where P_0 is the orientation polarization, which is derived from the expression $P_0 = P_{2\infty} - R_D$; R_D, the molar refraction of solute for the sodium D line, is given by $R_D = M_2[3\gamma v_1/(n_1^2 + 2)^2 + (n_1^2 - 1)(v_1 + \beta)/(n_1^2 + 2)]$.

RESULTS

Table 1 gives weight fractions, dielectric constants, specific volumes and the squares of the refractive indices, whilst the polarization data and dipole moments obtained from these measurements are given in Table 2.

Table 3 lists the values of μ_{calc}, μ_B(benzene), μ_D(dioxan), μ_{int}(benzene), μ_{int} (dioxan), σ and $\Delta\mu_{\text{vect}}$ ($\Delta\mu = \mu_D - \mu_B$, and $\Delta\mu_{\text{vect}}$ is the vectorially calculated value of $\Delta\mu$). The following equations were used to obtain μ_{calc}, μ_{int} and $\Delta\mu_{\text{vect}}$ values.

1. *Calculated moments* (μ_{calc})

$$\mu_{\text{calc}}^2 = \mu^2\text{NH}_2 + \mu^2\text{NO}_2 + 2\mu\text{NH}_2 \,.\, \mu\text{NO}_2 \,.\, \cos\alpha \,.\, \cos\beta \qquad (5)$$

where μNH$_2$ refers either to the dipole moment of 1- or 2- (Ref. 14) naphthylamine in benzene solution (1·49D and 1·77D respectively), whichever is appropriate for the particular compound under consideration. μNO$_2$ refers to the dipole moment of 1- or 2-nitronaphthalene in benzene solution (3·96D and 4·36D, Ref. 14, respectively). α is the angle that the amino group in the 1- and 2- positions makes with the C—N bond axis, and is assumed to be 48½° as in aniline. β is equal to 0°, 60° or 120° for substituents inclined at angles of 180°, 120° and 60° respectively in the plane of the naphthalene rings.

2. *Interaction moments* (μ_{int})

These were obtained by vector calculation of the differences between the observed moments in either benzene or dioxan solution and the calculated moments obtained in the previous section.

A definite direction must be assumed for the axis of this additional component to the moment. Smith and Walshaw assumed that both substituents make equal

TABLE 1. DIELECTRIC CONSTANT, SPECIFIC VOLUMES AND REFRACTIVE INDICES SQUARED DATA FOR MONO- AND DI-SUBSTITUTED NAPHTHALENE COMPOUNDS

Compounds	$10^7 w_2$	ϵ_{12}	v_{12}	n_{12}^2
1-Naphthylamine in dioxan	18630	2·2171	0·97247	2·01283
	31933	2·2195	0·97232	2·01887
	41658	2·2229	0·97220	2·01944
	57122	2·2288	0·97203	2·02053
	60268	2·2291	0·97198	2·02082
	66776	2·2315	0·97193	2·02119
1-Nitronaphthalene in benzene	5962	2·2785	1·14423	2·24358
	14996	2·2878	1·14392	2·24390
	25162	2·2979	1·14359	2·24423
	28595	2·3016	1·14342	2·24435
	40614	2·3136	1·14300	2·24473
	42843	2·3160	1·14297	2·24482
	61301	2·3350	1·14230	2·24540
3-Nitro-1-naphthylamine in dioxan	8826	2·2267	0·97257	2·01751
	17869	2·2455	0·97234	2·01813
	30070	2·2692	0·97204	2·01890
	42686	2·2946	0·97171	2·01972
	53581	2·3191	0·97146	2·02043
	57907	2·3265	0·97130	2·02073
	67679	2·3461	0·97107	2·02140
4-Nitro-1-naphthylamine in benzene*	6437	2·2874	1·14423	
	12538	2·3026	1·14391	
	13178	2·3044	1·14391	
	13930	2·3066	1·14390	
	15716	2·3102	1·14382	
	20544	2·3213	1·14375	
4-Nitro-1-naphthylamine in dioxan	14210	2·2571	0·97239	2·01720
	26765	2·2997	0·97203	2·01833
	39394	2·3417	0·97173	2·01941
	56980	2·4008	0·97124	2·02095
	64272	2·4263	0·97112	2·02174
	84777	2·4925	0·97056	2·02336
5-Nitro-1-naphthylamine in benzene	12797	2·2915	1·14388	2·24295
	13460	2·2931	1·14382	2·24298
	23893	2·3085	1·14340	2·24340
	38139	2·3310	1·14278	2·24396
	43918	2·3421	1·14255	2·24422
	80651	2·4023	1·14104	2·24576
5-Nitro-1-naphthylamine in dioxan	10821	2·2329	0·97247	2·01762
	23026	2·2622	0·97211	2·01792
	37607	2·2941	0·97179	2·01896
	48953	2·3201	0·97153	2·01987
	56036	2·3357	0·97129	2·02009
	60631	2·3465	0·97117	2·02061

* Because of the limited solubility of 4-nitro-1-naphthylamine in benzene the refractive indices were not measured in this solvent.

TABLE 1 contd

Compounds	$10^7 w_2$	ϵ_{12}	v_{12}	n_{12}^2
6-Nitro-1-naphthylamine in benzene	14336	—	1·14386	2·24355
	23873	2·3096	1·14356	2·24397
	29471	2·3193	1·14330	2·24420
	35508	2·3283	1·14302	2·24447
	38754	2·3342	1·14293	2·24459
	47428	2·3463	1·14260	2·24495
	50956	2·3518	—	2·24511
6-Nitro-1-naphthylamine in dioxan	12763	2·2336	0·97245	2·01738
	19292	2·2508	0·97237	2·01792
	23666	2·2573	0·97214	2·01819
	31326	2·2736	0·97203	2·01875
	42928	2·2973	0·97166	2·01958
	46629	2·3063	0·97151	2·01985
7-Nitro-1-naphthylamine in benzene	9655	2·2837	1·14403	2·24378
	16078	2·2916	1·14372	2·24406
	26157	2·3031	1·14339	2·22463
	28685	2·3060	1·14312	2·24478
	38513	2·3178	1·14281	2·24523
	43644	2·3238	1·14263	2·24547
	58353	2·3407	1·14190	2·24625
7-Nitro-1-naphthylamine in dioxan	10920	2·2264	0·97242	2·01762
	17550	2·2360	0·97228	2·01810
	32667	2·2592	0·97190	2·01927
	41049	2·2725	0·97170	2·01984
	47077	2·2820	0·97156	2·02025
	58363	2·2996	0·97127	2·02110
4-Nitro-2-naphthylamine in benzene	8119	2·2835	1·14391	2·24381
	21243	2·3011	1·14383	2·24450
	31016	2·3144	1·14269	2·24510
	39380	2·3248	1·14230	2·24553
	54169	2·3453	1·14145	2·24637
	66661	2·3620	1·14082	2·24703
	70964	2·3674	1·14056	2·24730
4-Nitro-2-naphthylamine in dioxan	10531	2·2227	0·97240	2·01779
	20022	2·2434	0·97212	2·01839
	34756	2·2687	0·97167	2·01938
	44629	2·2864	0·97136	2·01998
	58351	2·3081	0·97094	2·02092
	78693	2·3412	0·97028	2·02220
5-Nitro-2-naphthylamine in dioxan	10763	2·2287	0·97254	2·01760
	22436	2·2519	0·97219	2·01822
	29623	—	0·97216	2·01815
	22665	2·2522	0·97196	2·01853
	39485	2·2858	0·97178	2·01917
	50357	2·3077	0·97153	2·01980
	52553	2·3124	0·97140	2·02002

TABLE 1 (contd)

Compounds	$10^7 w_2$	ϵ_{12}	v_{12}	n_{12}^2
6-Nitro-2-naphthylamine in benzene*	9092	2·2923	1·14382	
	9498	2·2937	1·14379	
	13437	2·3018	1·14352	
	15941	2·3082	1·14335	
	18344	2·3138	1·14319	
6-Nitro-2-naphthylamine in dioxan	14786	—	0·97221	2·01799
	24136	2·2889	0·97208	2·01913
	34247	2·3265	0·97176	2·01958
	45404	2·3660	0·97155	—
	48503	2·3723	0·97151	2·02095
	59397	2·4141	0·97116	2·02238
	70094	2·4484	0·97090	2·02303
7-Nitro-2-naphthylamine in benzene	8781	2·2909	1·14405	2·24402
	11918	2·2979	1·14398	2·24406
	16041	2·3059	1·14377	2·24438
	19512	2·3130	1·14365	2·24448
	24341	2·3221	1·14341	2·24476
	35486	2·3433	1·14294	2·24533
7-Nitro-2-naphthylamine in dioxan	11095	2·2365	0·97242	2·01694
	26672	2·2812	0·97205	2·01789
	39319	2·3118	0·97173	2·01916
	52918	2·3600	0·97144	2·02002
	64571	—	0·97115	2·02078
	68078	2·4083	0·97107	2·02109
	78948	2·4258	0·97085	2·02181
8-Nitro-2-naphthylamine in dioxan	9312	2·2245	0·97264	2·01725
	20101	2·2407	0·97239	2·01791
	30006	2·2579	0·97218	2·01870
	46638	2·2816	0·97178	2·01992
	51195	2·2906	0·97166	2·02009
	55485	2·2951	0·97158	2·02058
	66109	2·3116	0·97130	2·02152

* Because of the limited solubility of 6-nitro-2-naphthylamine in benzene the refractive indices were not measured.

contributions to the effect and that these contributions are directed along the bonds linking the groups to the ring. The resultant contribution is taken as acting along an axis parallel to the line joining the ring carbon atoms carrying the substituents. The following equation takes this assumption into account

$$\mu_{\text{int}} = [\{\cos \Delta\, (\mu\text{NH}_2 \cos 48\tfrac{1}{2}^\circ + \mu\text{NO}_2)\}^2 + \mu^2_{\text{obs}} - \mu^2_{\text{calc}}]^{1/2} - \cos \Delta\, (\mu\text{NH}_2 \cos 48\tfrac{1}{2}^\circ + \mu\text{NO}_2) \quad (6)$$

where $\Delta = 60°$, $30°$ and $0°$ for ring substituents separated by angles of 60°, 120° and 180° respectively in the plane of the naphthalene rings. μ_{obs} refers to the dipole moments observed in either benzene or dioxan solutions and the other terms have their previous significance.

TABLE 2. POLARIZATION DATA FOR THE MONO- AND DISUBSTITUTED NAPHTHALENE COMPOUNDS IN BENZENE AND DIOXAN SOLUTION

Compound	Solvent	α	β	γ	$P_{2\infty}$ (cm³)	R_D (cm³)	P_0 (cm³)	μ (D)
1-Naphthylamine	D	3·2136	−0·11615	0·69697	111·03	49·10	61·93	1·74
1-Nitronaphthalene	B	10·1557	−0·35175	0·32851	371·85	51·10	320·75	3·96
3-Nitro-1-naphthylamine	D	20·2686	−0·25268	0·64712	667·33	56·33	611·00	5·47
4-Nitro-1-naphthylamine*	B	23·9887	−0·38619	—	891·52	63·23	828·29	6·40
4-Nitro-1-naphthylamine	D	33·4517	−0·26152	0·86209	1075·59	63·23	1012·36	7·04
5-Nitro-1-naphthylamine	B	15·8077	−0·41953	0·41761	600·11	54·92	545·19	5·16
5-Nitro-1-naphthylamine	D	22·5436	−0·25899	0·60994	737·53	54·60	682·93	5·78
6-Nitro-1-naphthylamine	B	15·6852	−0·39197	0·42400	597·32	56·70	540·62	5·14
6-Nitro-1-naphthylamine	D	20·6649	−0·28821	0·70029	677·70	56·45	621·25	5·51
7-Nitro-1-naphthylamine	B	11·7263	−0·43196	0·50524	454·96	57·41	397·55	4·41
7-Nitro-1-naphthylamine	D	15·4923	−0·24780	0·73209	519·52	59·45	460·07	4·74
4-Nitro-2-naphthylamine	B	13·2889	−0·52872	0·55050	504·84	53·70	451·14	4·70
4-Nitro-2-naphthylamine	D	16·9563	−0·30002	0·64053	562·08	53·85	508·23	4·99
5-Nitro-2-naphthylamine	D	19·9754	−0·26044	0·59417	657·82	54·16	603·66	5·42
6-Nitro-2-naphthylamine*	B	22·1981	−0·69067	—	811·09	66·49	744·60	6·04
6-Nitro-2-naphthylamine	D	34·3593	−0·24413	0·93378	1104·67	66·49	1038·18	7·13
7-Nitro-2-naphthylamine	B	20·5016	−0·42471	0·50397	765·95	57·77	708·18	5·89
7-Nitro-2-naphthylamine	D	27·9937	−0·23463	0·71619	907·82	59·54	848·28	6·44
8-Nitro-2-naphthylamine	D	15·9916	−0·23023	0·73410	535·94	60·36	475·58	4·82

* Refractive indices not measured in benzene solution. The R_D value obtained for the dioxan solution has, therefore, been used.

TABLE 3. DIPOLE MOMENT (IN DEBYE UNITS) AND σ DATA FOR MONO- AND DISUBSTITUTED NAPHTHALENE COMPOUNDS

Naphthalene derivative	μ_{calc}	μ_B (benz)	μ_B (lit)	μ_{int} (benz)	μ_D (diox)	μ_D (lit)	μ_{int} (diox)	$\Delta\mu_{vect}$	σ (nitro-substituents)[4]	σ (nitro-substituents)[7]
$1\text{-}NH_2$		1·49			1·74			0·35		
$2\text{-}NH_2$			1·77[14]		2·10			0·46		
$1\text{-}NO_2$		3·96								
$2\text{-}NO_2$			4·36[14]							
$3\text{-}NO_2\text{-}1\text{-}NH_2$	5·05		5·14[14]	0·09	5·47		0·45	0·36	0·63	0·71
$4\text{-}NO_2\text{-}1\text{-}NH_2$	5·07	6·40	6·38[13]	1·35	7·04	6·97[14]	2·00	0·65	1·21	0·84
$5\text{-}NO_2\text{-}1\text{-}NH_2$	5·07	5·17	5·22[14]	0·09	5·78		0·72	0·63	0·39	0·52
$6\text{-}NO_2\text{-}1\text{-}NH_2$	5·05	5·14		0·09	5·51		0·50	0·41	0·34	0·41
$7\text{-}NO_2\text{-}1\text{-}NH_2$	4·11	4·41		0·43	4·74		0·88	0·45	0·44	0·53
$4\text{-}NO_2\text{-}2\text{-}NH_2$	4·84	4·70	4·62[14]	−0·15	4·99		0·16	0·31	0·58	0·71
$5\text{-}NO_2\text{-}2\text{-}NH_2$	4·84		5·03[14]	0·21	5·42		0·65	0·44	0·37	0·41
$6\text{-}NO_2\text{-}2\text{-}NH_2$	5·69	6·04	5·14[18]	0·36	7·13	7·10[14]	1·47	1·11	0·52	0·41
$7\text{-}NO_2\text{-}2\text{-}NH_2$	5·22	5·89		0·72	6·44		1·31	0·59	0·34	0·36
$8\text{-}NO_2\text{-}2\text{-}NH_2$	3·76		4·47[14]	0·95	4·82		1·39	0·44	0·48	0·53

3. $\Delta\mu_{vect}$ *values*

These were obtained from the equation

$$\Delta\mu_{vect} = \mu_{int}(\text{dioxan}) - \mu_{int}(\text{benzene}) \qquad (7)$$

DISCUSSION

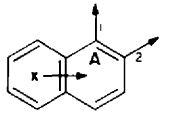
Before discussing the relationships between the μ_{int} values and σ constants the difference in the group moments of substituents in benzene and in the 1- and 2-positions in naphthalene will be considered. It can be seen from Table 4 that the group moments of 2-substituted naphthalenes are greater than those for the 1-substituted isomers, which are approximately equal to the values for the corresponding

TABLE 4. DIPOLE MOMENTS IN BENZENE SOLUTION

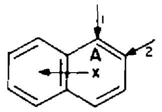
Substituent	Benzene	1-Naphthalene	2-Naphthalene
NH_2	1·53	1·49	1·77D
NO_2	4·01	3·96	4·36D

benzene compounds.[15] The greater dipole moments for the 2-substituted naphthalene may be caused by one or both of the following factors:

(i) The contribution (xD) to the dipole moment for both −M and +M substituents by the unsubstituted ring will have a greater effect in the case of the 2-substituted compounds as may be deduced from the direction of the vectors in the following diagram:



For NO_2 substitution in ring A



For NH_2 substitution in ring A

(ii) The peri-hydrogen atom may cause twisting of the 1-substituents out of the plane of the aromatic system with consequent loss in mesomeric contribution. This reason has been put forward by Elliott and Mason[16] to explain the low value for the HNH angle in 1-naphthylamine. Krueger[17] has also stated that the direction of the displacement of the graph relating ν_{as} to ν_s for substituted 1-naphthylamines compared with that for the substituted 2-naphthylamines and *m*- and *p*-anilines is consistent with more sp^3 character in the 1-amino group and has been ascribed to interference by the peri-hydrogen atom.

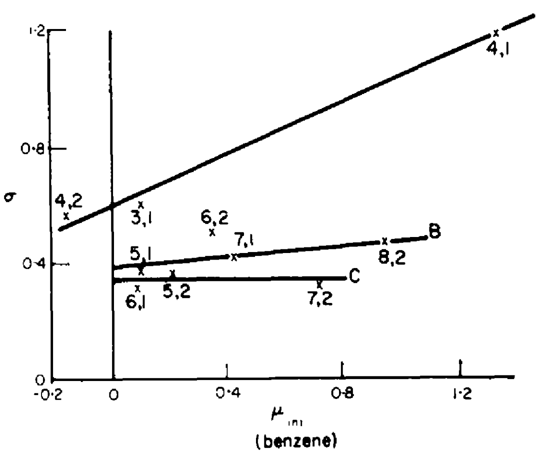


FIG. 1. Plot of μ_{int} (benzene) vs. the corresponding σ value for the nitronaphthylamines.

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[15] L. G. Wesson, *Tables of Electric Dipole Moments*. Technology Press, Massachusetts Institute of Technology (1947).

[16] J. J. Elliott and S. F. Mason, *J. Chem. Soc.* **1275** (1959).

[17] P. J. Krueger, *Spectrochim. Acta* **19**, 705 (1963).

As regards the correspondence of the dipole moments of the 1-substituted naphthalene compounds with those of the same substituent in benzene it would seem that the effects of the peri-hydrogen atom are almost balanced by the contribution from the unsubstituted ring.

In Fig. 1 the σ values obtained by Bryson[4] from the pK_a's of the nitronaphthylamines in water at 25° have been plotted against the μ_{int}(benzene) values and in Fig. 2

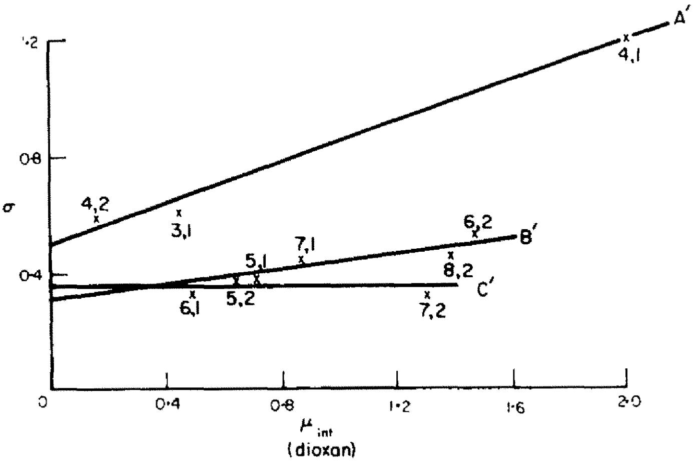


FIG. 2. Plot of μ_{int} (dioxan) vs. the corresponding σ value for the nitronaphthylamines.

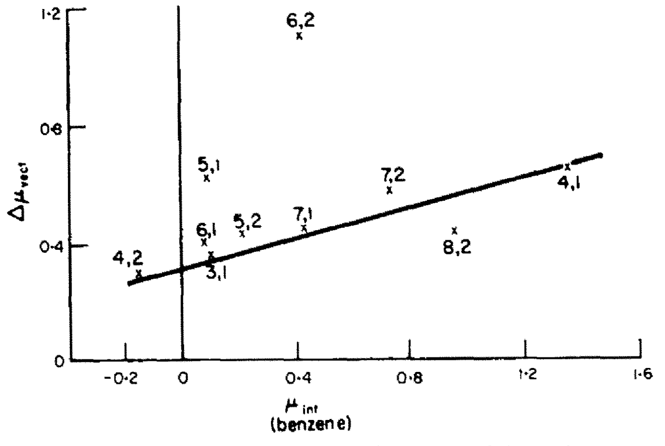


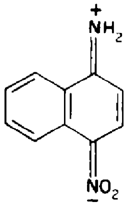
FIG. 3. Plot of $\Delta\mu_{vect}$ vs. μ_{int} (benzene) for the nitronaphthylamines in relation to the line for the corresponding plot of a number of *m*- and *p*-substituted anilines.

the same σ values are plotted against μ_{int}(dioxan). In both Figs. the points fall on three lines. The striking features which emerge are that the compounds on lines A and A′ are homonuclear nitronaphthylamines, on B and B′ heteronuclear nitronaphthylamines which have ionic resonance forms, and on C and C′ heteronuclear nitronaphthylamines which have no ionic resonance forms.

The apparent relationship between σ and dipole moment data for the nitronaphthylamines will now be explored in more detail.

Homonuclear nitronaphthylamines

The μ_{int} values in both solvents decrease in the order 4-NO_2-1- $\gg$ 3-NO_2-1- $>$ 4-NO_2-2- naphthylamines. The μ_{int} of 4-NO_2-1-naphthylamine in benzene is appreciably greater than that for *p*-nitroanaline (1·08D)[1] and is to be associated with a significant contribution from the resonance form:



I

In dioxan the μ_{int} of this isomer increases by 0·65D which is strong support for the contributions of such a species.

With regard to 3-nitro-1-naphthylamine interaction between the 1-NH_2- and the 3-NO_2- must be small, and the effects produced by the substituents on each other must be mainly inductive. This is borne out by its moment in benzene being only about 0·2D greater than that of *m*-nitroaniline (4·91D) which was shown by Smith and Walshaw[1] to have negligible (or no) mesomeric interaction between the groups. In fact, the interaction moments for the 3-nitro-1-naphthylamine and 4-nitro-2-naphthylamine isomers in benzene are lower than that for *m*-nitroaniline[1] (0·18D). This parallels the observations based on σ data for Bryson[4] who concluded that the inductive effect of the nitro group is decreased in the two former compounds compared with its effect in the benzene analogue. The larger μ_{int} value for the 3-nitro-1-naphthylamine compared with the 4-nitro-2-isomer also agrees with Bryson's results.

Heteronuclear substituents in quinonoid positions

The order of interaction between the two substituents as indicated by the μ_{int} values is

$$6\text{-}NO_2\text{-}2\text{-} > 8\text{-}NO_2\text{-}2\text{-} > 7\text{-}NO_2\text{-}1\text{-} > 5NO_2\text{-}1\text{- in dioxan}$$

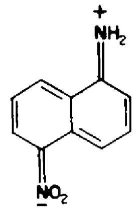
In benzene the position of 6-NO_2-naphthylamine may be doubtful since the point for this compound does not lie on the appropriate line in Fig. 1. However, the order for the other isomers is certainly

$$8\text{-}NO_2\text{-}2\text{-} > 7\text{-}NO_2\text{-}1\text{-} > 5\text{-}NO_2\text{-}1$$

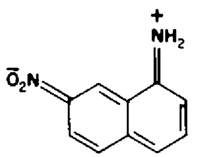
The most significant features to be obtained from this type of naphthylamine emerge from the μ_{int} data and are:

(i) The μ_{int} of the 6-NO_2-2- in dioxan is the closest in magnitude to that of the 4-NO_2-1- and must be related to the ionic resonance form II

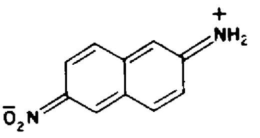
(ii) Apart from the 7-NO_2-2- (see later) and 4-NO_2-1- the molecules in this group have the largest μ_{int} values in dioxan. It is interesting to note that mesomerism might be expected to be greater in 7-nitro-1-naphthylamine than in the 5-NO_2-1- isomer since the contributing quinonoid form in the latter case has a doubly *ortho* quinonoid structure (V) whereas an *ortho-para* quinonoid structure (IV) contributes to the resonance state of the former isomer.



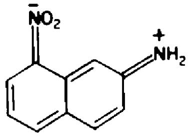
V



IV



II



III

Similarly, the doubly *para* quinonoid contribution (II) to the resonance state of the 6-NO_2-2-isomer suggests that the interaction between the substituents might be greater in this compound than in the 8-NO_2-2- isomer where the corresponding contribution has an *ortho-para* quinonoid structure (III).

Although the σ values lead to the same order as that for μ_{int}(dioxan) each one of these σ values is appreciably less than that for the 3-NO_2-1-, a compound in which only inductive interactions are significant between the groups. The μ_{int} in dioxan, though, would seem well suited for detecting such conjugation. Thus, it would appear significant that both the μ_{int} in benzene and the σ values indicate no significant contributions of the resonance form V—the μ_{int} in benzene being of the same order as that for the 3-NO_2-1- isomer, whereas the μ_{int} dioxan is 0·27D greater than that for the 3-NO_2-1- compound. Evidently, this indicates that the ionic structure V becomes more stable in dioxan as a result of the hydrogen bonding.

Heteronuclear substituents in non-quinonoid positions

The σ values for the 6-NO_2-1-, 5-NO_2-2- and 7-NO_2-2- naphthylamines are amongst the lowest for the nitronaphthylamines. For the 6-NO_2-1- the μ_{int} values are of the same order as for the 3-NO_2-1- indicating that the interaction between the 1-NH_2- and the 6-NO_2- groups is small. The μ_{int} of the 5-NO_2-2- in dioxan is less than that of any of the isomers with substituents in quinonoid positions—unlike the 7-NO_2-2NH_2- which has a μ_{int} in dioxan greater than that of the 5-NO_2-1- and 7-NO_2-1-.

For the 6-NO_2-1- and 7-NO_2-2- isomers Bryson[4] has analysed his σ values in terms of inductive and mesomeric contributions. He concludes that for these two compounds there is a considerable mesomeric contribution and that this may indicate the extent to which conjugation of the nitro group with its ring is effective in the adjacent ring.

As regards its high μ_{int} values the 7-NO_2-2- at first sight appears an anomaly. However, in this compound it is to be noted that there is an absence of a peri-hydrogen effect on both the —NO_2 and —NH_2 groups and the vector contributions from the two dipoles tend to support each other (see p. 848). Both these factors would lead to a higher μ_{int} in benzene as a result of increased conjugation of groups with the π-electron system and probably an enhanced π-inductive effect. In support of such increased mesomerism is the appreciable increment of 0·59D of μ_{int} dioxan over μ_{int} benzene which reflects an increased interaction of the NH_2 group with the π electron system compared with that for example in the 3-NO_2-1- isomer where the difference is only 0·36D.

Application of data to the Smith and Walshaw equation

Smith and Walshaw[1] have shown that a relationship exists between μ_{int} and $\Delta\mu_{vect}$ for various *m*- and *p*-substituted anilines. This relationship is expressed by Eqn 8.

$$\Delta\mu_{vect} = 0{\cdot}255\ \mu_{int(Benz)} + 0{\cdot}33 \tag{8}$$

Fig. 3 gives a plot of $\Delta\mu_{vect}$ against μ_{int} (benzene) for the nitronaphthylamines. It can be seen that most of the points lie close to the line which represents Eqn 8. The three homonuclear isomers obey this relationship. Thus, although the μ_{int}(benzene) values for these compounds differ from those of the analogous benzene compounds, (i.e. *m*- and *p*-nitroaniline) it would appear that the change in solvent from benzene to dioxan has the same relative effect on the interaction between the substituents.

The 6-NO_2-2H_2 and the 5-NO_2-1NH_2 isomers show the greatest deviation from Eqn 8. Both deviations can be explained if it is assumed that the increases in the quinonoid contributions to the resonance states on the formation of intermolecular hydrogen bonds with dioxan are relatively greater in these compounds than in *p*-nitroaniline and 4-nitro-1-naphthylamine. This assumption seems to be reasonable in view of the fact that the mutual conjugation is appreciable for the latter two compounds even in benzene solution. Thus, although the formation of intermolecular hydrogen bonds with dioxan will cause an increase in the contribution of the homonuclear quinonoid form this increase will probably not have such a marked effect as that observed for the heteronuclear quinonoid compounds where the ionic resonance contribution is relatively small in benzene solution. The latter is supported by the study of the IR spectra of the nitronaphthylamines in carbon tetrachloride (a relatively non-interacting solvent) carried out by Hathway and Flett[18] who concluded that for 5-nitro-1- the contribution of structure V is relatively unimportant. In addition, Krueger[17] has calculated the N—H stretching force constants for these compounds in the same solvent. His results indicate that the 5-nitro substituent has a smaller effect on the amino group in the 1-position than a nitro group in any other position except for 8-nitro-1-naphthylamine where proximity effects are important. Bryson's[4] IR studies also show that a considerable increase in the symmetric and asymmetric N—H_2 stretching frequencies accompanies a change in the substituent from OH to NO_2 in 7-substituted-1-naphthylamines whereas the 5-substituted-1-naphthylamines show virtually no change. Thus, even the fact that the 7-nitro-1-naphthylamine—a heteronuclear isomer with a quinonoid form—obeys the relationship may be accounted for by a greater contribution of form IV than the corresponding form V for the 5-NO_2-1-naphthylamine in benzene solution and, hence, relatively a smaller increment of the ionic resonance form in dioxan. It may be significant that the μ_{int} (benzene) for the 7-nitro-1-naphthylamine is slightly greater than that for the 6-nitro-2-naphthylamine whereas in dioxan the latter has a μ_{int} appreciably greater.

The points for the three heteronuclear nitronaphthylamines with substituents at

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[18] D. E. Hathway and M. St. C. Flett, *Trans. Faraday Soc.* **45**, 318 (1949).

120° to each other and in non-quinonoid positions lie slightly above the line representing Smith's and Walshaw's equation. The direction of this deviation indicates that the interaction moment in dioxan is increased relative to that for the homonuclear "*meta*" substituted isomers and the *meta*-substituted anilines. This would suggest that the increased mesomerism on intermolecular hydrogen bond formation with dioxan is relatively greater in these heteronuclear compounds. Bryson's results[4] also indicate that the mesomeric contributions to the substituent effects in these compounds is relatively greater than those in the analogous anilines and homonuclear naphthylamines.

The 8-NO_2-2-naphthylamine point lies slightly below the Smith and Walshaw line. This may be related to a significant contribution of the quinonoid form when in benzene solution—reflected in the high μ_{int} (benzene) value—and relative to 5-NO_2-1- and 6-NO_2-2-naphthylamines a smaller increment of such a form in dioxan solution.

EXPERIMENTAL

Materials. Catarax benzene was shaken with several batches of conc. H_2SO_4 until no darkening of the acid occurred. After being washed with distilled water the benzene was dried over KOH pellets. An initial fractional distillation from Na through a small column was followed by a similar distillation through a 20-plate column. The benzene was stored over Na wire in well-closed amber containers until required for use. ($d_{4^\circ}^{25^\circ}$ 0·87378, $n_D^{25^\circ}$ 1·49778).

A. R. dioxan was purified by the method of Eigenberger[19] by refluxing for 12 hr with N HCl, whilst a slow stream of nitrogen was passed to remove aldehydes. The product was dried over two successive portions of KOH pellets and then refluxed with Na until the latter remained bright. It was finally fractionally distilled from Na through a 20-plate column and stored in a similar manner to the benzene. ($d_{4^\circ}^{25^\circ}$ 1·02800, $n_D^{25^\circ}$ 1·42020).

1-Nitronaphthalene (m.p. 58°) was purified by the method of Fierz-David and Sponagel.[20]

1-Naphthylamine (m.p. 49·3°). In order to ensure that all the 2-isomer was absent, 1-naphthylamine was prepared from 1-nitronaphthalene, from which it is easier to remove the 2-isomer by the above purification procedure, by reduction with Swedish iron powder and HCl.

The mononitronaphthylamines were provided by Dr. E. R. Ward and were purified by chromatography on alumina followed by crystallization. The m.ps agreed with those recorded in the literature.

Physical measurements

Dielectric constants. These were measured at a frequency of 1 Mps using a heterodyne beat apparatus based on the circuit described in Weissberger's *Physical Methods of Organic Chemistry*[21] but incorporating a cathode-ray oscilloscope to detect the balance point. The dielectric constant cell of Sayce-Briscoe type, as modified by Few *et al.*,[22] had a volume of ca. 12 cm^3 and a capacity of ca. 100 $\mu\mu$F when filled with air.

Densities. A pyknometer similar to that described by Cumper *et al.*[23] was used and the weights were reproducible to 0·1 mg.

Refractive indices. These were measured on a Bellingham and Stanley refractometer of the Pulfrich type, reading to 0·00001. All measurements were carried out in a large thermostat tank maintained at 25·00 ± 0·01°, the water being circulated through the refractometer by means of an efficient pump.

Acknowledgments—We are indebted to the D.S.I.R. for an award (J.H.R.) and to Dr. E. R. Ward for supplying the nitronaphthylamines. We express our gratitude to Mr. L. P. Priestley, Head of the School of Chemistry, College of Technology, Leicester, where the practical work was carried out, and to Mr. A. Clarke for technical assistance.

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[19] E. J. Eigenberger, *J. Prakt. Chem.* **130,** 75 (1931).

[20] H. E. Fierz-David and R. Sponagel, *Helv. Chim. Acta* **26,** 98 (1943).

[21] *Physical Methods of Organic Chemistry* (Edited by A. Weissberger) Vol. 1; p. 1638. Interscience, New York (1949).

[22] A. V. Few, J. W. Smith and L. B. Witten, *Trans. Faraday Soc.* **48,** 211 (1952).

[23] C. W. H. Cumper, A. I. Vogel and S. Walker, *J. Chem. Soc.* 3621 (1956).