Notes

Solvent Effect on the Dipole Moments of Some N-Substituted Maleimides

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Dipole moments of six N-substituted maleimides have been
determined in benzene and dioxane at 30°C. The apparent
solution moments obtained in benzene are found to be signifi-
cantly higher than those determined in dioxane indicating a
strong solute-solvent interaction in the former case.

Solute-solvent interactions in the maleimide mole-
cule and its N-substituted derivatives have been
intensively studied by Bryce-Smith *et al.*[1,2] using
the NMR technique. The large upfield shifts of
the ethylenic protons for the maleic anhydride
and maleimide molecules were attributed to a 1:1
exospecific association of the solute and the ben-
zene molecules. So, it seemed worthwhile to de-
termine the dipole moments of some N-aryl der-
ivatives of maleimide in benzene and another
non-polar solvent, namely dioxane, in order to
compare molecular interactions of maleimides
with different non-polar solvents.

(I)
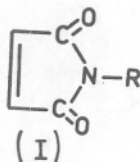
(a) R = C_6H_5; (b) R = 2-ClC$_6$H$_4$; (c) R = 4-ClC$_6$H$_4$;
(d) R = 4-NO$_2$C$_6$H$_4$; (e) R = 2-CH$_3$C$_6$H$_4$; (f) R = 1-naph-
thyl.

N-Arylmaleimides (Ia-f) were prepared accord-
ing to the procedure originally developed by
Searle[3]. The products prepared were crystallized
twice from ethanol and dried *in vacuo*. The melt-
ing points and spectral analyses of the compounds
were in satisfactory agreement with the literature
values[3].

Benzene and dioxane (BDH) were purified ac-
cording to recommended procedures[4]. Dilute so-
lutions of the maleimides Ia-f in benzene and di-
oxane were prepared with weight fractions rang-
ing from 10^{-3} to 10^{-2}. The dielectric constants,
densities, and refractive indices were measured at

30°C, and the calculations of dipole moments
were made as described earlier[5].

On the basis of precisions in the measurements
of dielectric constants (± 0.0005), densities
(± 0.0001), refractive indices (± 0.0001), and so-
lution concentrations ($\pm 0.02\%$), the dipole mo-
ment values obtained are believed reliable to
± 0.03 D.

Polarization and dipole moment data of N-aryl-
maleimides (Ia-f) in benzene and dioxane at 30°C
are summarized in Table 1. The average values of
the dipole moments obtained by the Hedestrand[6]
and the Guggenheim[7] methods in both solvents
and the dipole moment difference ($\Delta \mu$) are col-
lected in Table 2.

As is observed from Table 2, the dipole mo-
ments of compounds Ia-f are markedly higher in
benzene than those in dioxane. These findings
confirm specific association between the malei-
mide and the benzene molecules. The order in
which the difference ($\Delta \mu = \mu_{benzene} - \mu_{dioxane}$)
decreases is: $I_d > I_b > I_a > I_c > I_e > I_f$.

NMR spectral measurements made by Bryce-
Smith *et al.*[8] on solutions of N-substituted malei-
mides in carbon tetrachloride and benzene
showed large solvent-induced chemical shifts
($\Delta = \delta_{CCl_4} - \delta_{C_6H_6}$) for the solute ethylenic pro-
tons. Their results were confirmed by UV spectral
evidence[9] which showed that complexation oc-
curred with the aromatic solvent.
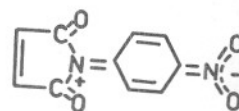
It is well known that the ethylenic double bond
in the imide ring of the maleimide molecule is an
electron deficient site, mainly due to the presence
of the two active electron-acceptor CO groups in
the same ring. The electrophilic character of the
ethylenic bond might be affected by the nature
and location of the substituent present in the phe-
nyl group (Ib-Ie). Thus, for the *p*-nitrophenyl der-
ivatives (Id), the electron deficiency of the ethyl-
enic bond is increased owing to the *p*-quinonoid
structure formation in which the lone pair of elec-
trons on the imide nitrogen atom are given to the
double bond connecting the phenyl group. This in
turn leads to a stronger interaction between the
ethylenic bond and the π-electron cloud of the
benzene molecule, so that $\Delta \mu$ for this compound

Table 1 — Polarization Data from Measurements on N-Arylmaleimides (Ia-f) at 30°C

Comp.	D^P2 (cm³)	Hedestrand				Guggenheim		
		$P_{2\infty}$	α	β	μ	$(\Delta/W_2)_{W_2\to 0}$	γ	μ
				In Benzene				
Ia	63.21	163.98	3.65	0.206	2.23	3.188	0.460	2.26
Ib	72.96	242.28	4.91	0.256	2.88	4.43	0.484	2.92
Ic	78.83	304.27	6.42	0.218	3.33	5.87	0.547	3.36
Id	72.56	1024.03	23.74	0.334	6.84	23.17	0.569	6.84
Ie	57.83	129.93	2.36	0.229	1.88	2.13	0.224	1.92
If	78.87	175.36	2.86	0.256	2.18	2.38	0.471	2.23
				In Dioxane				
Ia	50.45	96.38	1.97	0.170	1.49	1.712	0.257	1.49
Ib	56.54	114.77	2.11	0.283	1.69	1.713	0.398	1.69
Ic	58.38	220.23	4.98	0.171	2.82	4.962	0.024	2.90
Id	63.01	615.37	15.71	0.198	5.50	15.501	0.205	5.50
Ie	46.30	102.61	1.98	0.219	1.59	1.643	0.338	1.58
If	61.84	133.02	2.12	0.134	1.87	1.934	0.190	1.87

would be greater than that for the parent unsubstituted phenyl compound (Ia) as is experimentally observed. Also, the measured μ of this compound in benzene would be (as is the case) greater than that measured in dioxane. On this basis, the difference $\Delta\mu = \mu_{benzene} - \mu_{dioxane}$ can be wholly attributed to the π-interaction with the benzene molecule.

For the *p*-chloro derivatives (Ic), the mesomeric effect associated with the lone pair of electrons on the chlorine atom is slightly more than to be outweighed by the inductive effect. Consequently, the electrophilic character of the ethylenic bond would be deaccentuated with respect to that of the N-phenylmaleimide (Ia). This is borne out by the observation that $\Delta\mu$ of the *p*-chloro derivative is only 0.48 D compared to 0.75 D for Ia.

Owing to steric considerations, the phenyl ring would be more or less non-planar with the imide ring for the compound 2-chlorophenyl maleimide (Ib), and consequently, the inductive effect will be the only factor leading to a residual negative charge on the chlorine atom and an equivalent positive charge on the imide nitrogen. As a consequence of such effect, the electrophilic character of the ethylenic bond will increase, so that stronger specific interaction with the benzene molecule might be anticipated; that is to say, $\Delta\mu$ for the 2-chloro derivative would be much higher than that for the 4-chloro derivative. This is in harmony with the results obtained, the values of $\Delta\mu$

Table 2 — Average Dipole Moments Measured in Benzene and Dioxane and Their Difference ($\Delta\mu$)

Compound	$\mu_{dioxane}$	$\mu_{benzene}$	$\Delta\mu$
Ia	1.49	2.24	0.75
Ib	1.69	2.90	1.21
Ic	2.86	3.34	0.48
Id	5.50	6.84	1.34
Ie	1.58	1.90	0.32
If	1.88	2.20	0.32

of the 2- and 4-chloro derivatives being 1.21 and 0.48 D, respectively.

Conversely, the electron donating character of the methyl substituent in Ie, and the steric interactions of the 2-methylphenyl and 1-naphthyl substituents in Ie and If, respectively, which lead to the non-planarity with the rest of the molecule, decrease the extent of the residual positive charge on the imide nitrogen. Consequently $\Delta\mu$ is expected to be smaller for Ie and If as can be seen from Table 2.

References

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