

THE DEPENDENCE OF PULSE HEIGHT ON THE MOLECULAR STRUCTURE OF
THE SOLVENT AND FLUOR IN ORGANIC SCINTILLATORS

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Recent papers by the authors (1) have shown that a correlation exists between pulse height (β and γ radiation) and the molecular structure of the solvent and fluor in plastic and liquid scintillators. The purpose of the present paper is to review some of the published material and to extend this correlation by presenting some recent results.

It is known that in order to have an efficient solid or liquid scintillator a conjugated double bond system is necessary. This suggests that electron mobility and electron density are important factors in the absorption of energy which can be potentially emitted as light. The electrons in the conjugated double bond system may also be important in the transfer of this energy possibly by a π bond overlap between the solvent and the solute (1). Dipole-dipole interactions might also be a factor in the transfer of energy from the solvent to the solute and this would be favored by electron displacements within the molecule. Therefore, it is reasonable to expect that a suitable parameter which characterizes electron density distribution in a solvent or fluor molecule would bear some relation to the observed pulse height.

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For the aromatic systems used in this work it was possible by means of the Hammett (2) or Taft sigma (σ) values (3) to place a relative numerical value on the extent to which the substituents either donate or withdraw electrons from the benzene ring as compared to the hydrogen atom. Substituents donating electrons to the benzene ring have a negative sigma value and substituents withdrawing electrons have a positive sigma value.

Taft (3) has recently shown that the Hammett sigma (σ) value can be divided into inductive (σ_I) and resonance (σ_R) components such that $\sigma = \sigma_I + \sigma_R$.

The object of this paper is to determine whether the R.P.H. versus σ correlation can be generally applied to plastic, liquid and crystalline scintillators. The dependence of pulse height on the molecular structure of the aromatic solvent (plastic, liquid or crystalline) and fluors was studied by using ring substituted aromatic solvents and fluors with substituents which differ greatly in their ability to either donate electrons to or withdraw electrons from the aromatic ring.

RESULTS

I. Plastic Scintillators

A. The Effect of Solvent Structure

Plastic scintillators were prepared from a series of substituted styrenes whose substituent groups differed considerably in electronegativity. Paraterphenyl at 3% by weight and 0.05% POPOP were used throughout as the primary fluors and waveshifter, respectively.

The values of the relative pulse heights and σ , σ_I and μ , the dipole moment, for the ring substituents used on the styrene monomers which produced plastics with good optical properties are given in Table 1 and are plotted in Figures 1, 2 and 3 respectively.

TABLE 1. RELATIVE PULSE HEIGHT (α , β , γ RADIATION), SIGMA VALUES AND DIPOLE MOMENTS OF SUBSTITUTED STYRENE PLASTIC SCINTILLATORS^a

Styrene Substituent	R.P.H. + 2			Reference for σ , σ_I	σ	σ_I	μ
	α	β	γ				
None	15	39	39		0	0	0
Methyl	22	45	44	7,8	-0.16	-0.045	0.4 (4)
Mixed dimethyl	25	53	-				
3,4-Dimethyl	-	58	52	7,8	-0.23	-0.090 ^b	-
2,4-Dimethyl	-	61	55	7,8	(-0.32) ^c	-0.090 ^b	-
2,5-Dimethyl	-	54	-	7,8	(-0.23) ^c	-0.090 ^b	-
p-Isopropyl	-	43	-	12,7	-0.151	-0.0563	-
p-Ethyl	-	39	-	12,7	-0.151	-0.0517	-
p-Benzyl	-	38	-	7	-	+0.036	-
p-Methoxy	6	24	20	7,8	-0.26	+0.25	1.28 (5)
p-Chloro	0	2.5	0	7,8	+0.226	+0.47	1.73 (6)
m-Chloro	0	1.8	0	7,8	+0.373	-0.47 ^d	-

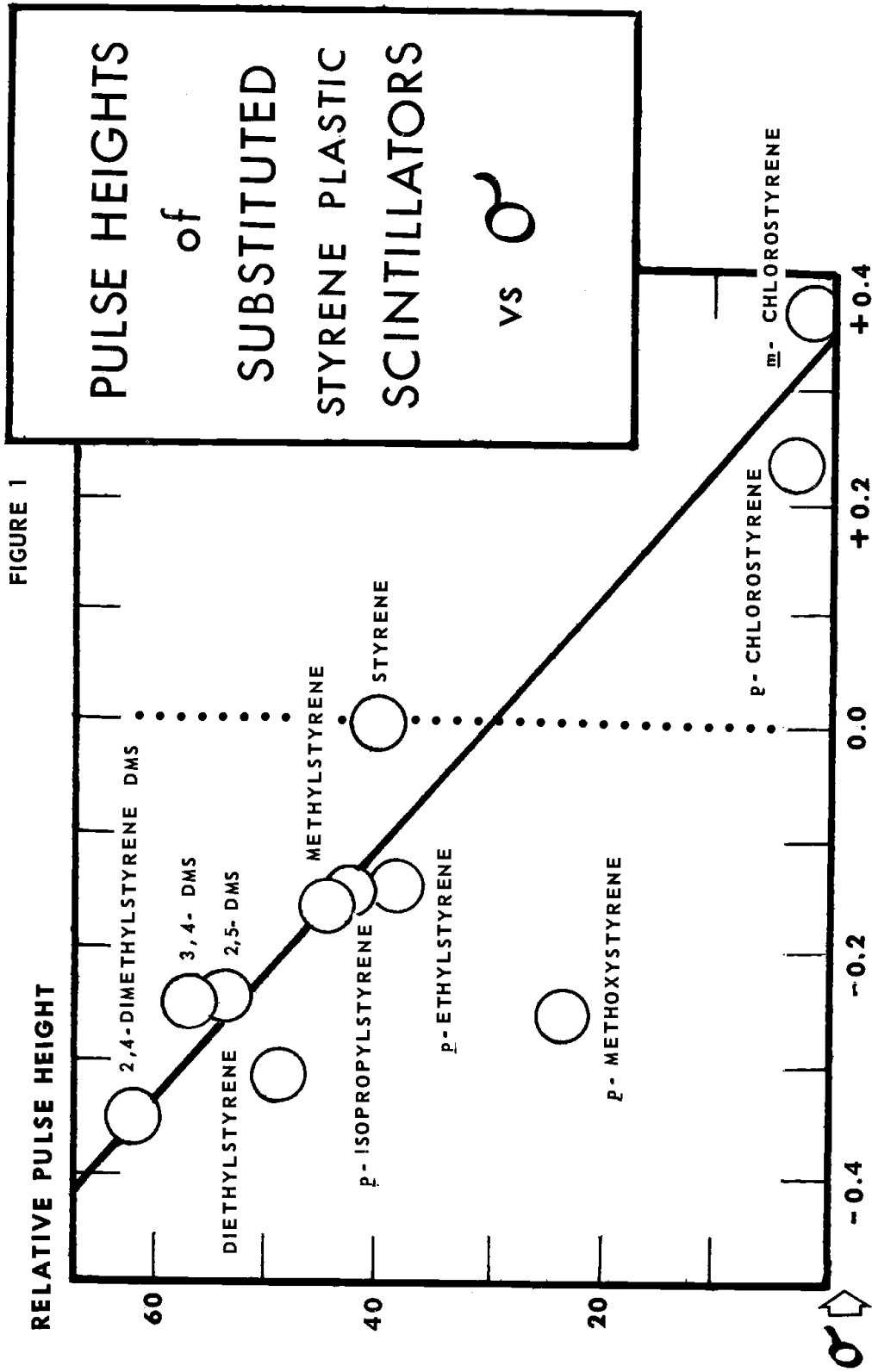
^aResults for β and γ radiation are presented in reference 1.

^bFor disubstituted styrenes the σ_I was obtained by taking the sum of the σ_I

for two methyl groups.

^cValues obtained by assuming that the o-methyl and p-methyl values are the same and that the values are additive.

^d σ_I was assumed to be the same as for p-chloro substituent.



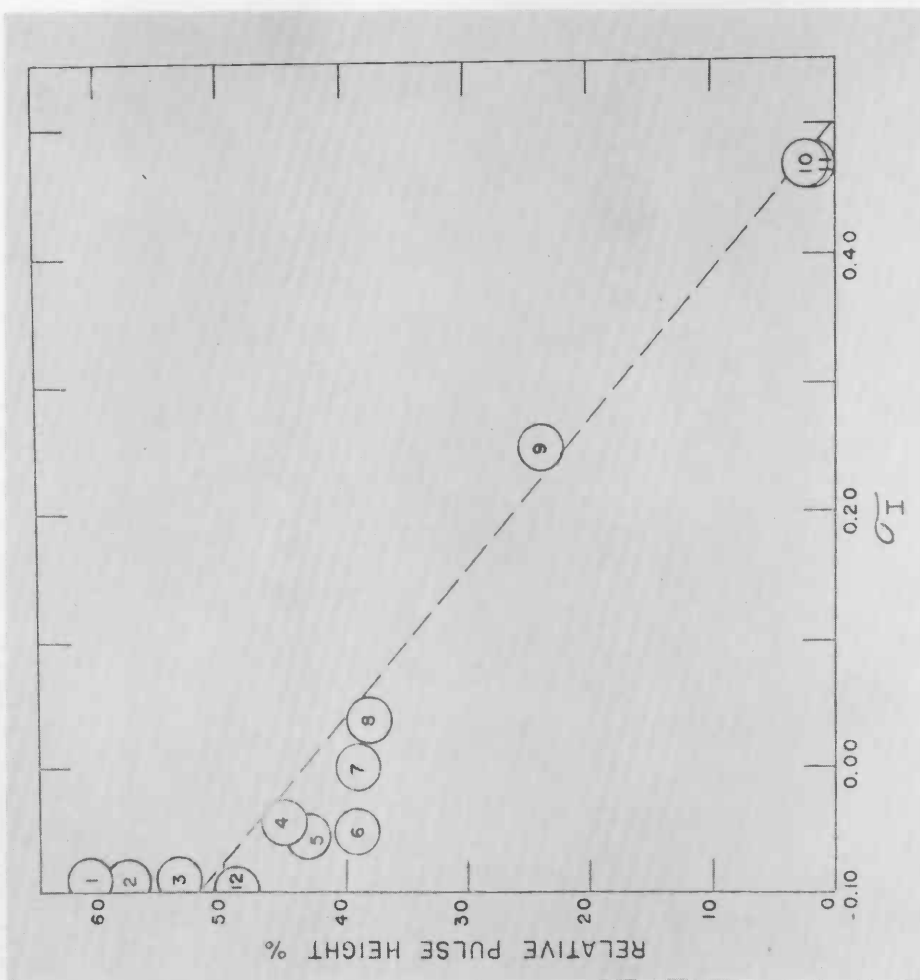


Figure 2. Pulse heights of substituted styrene plastic scintillators versus σ_I . (1) 2,4-DMS, (2) 3,4-DMS, (3) 2,5-DMS, (4) Methylstyrene, (5) p-isopropylstyrene, (6) p-ethylstyrene, (7) styrene, (8) p-benzylstyrene, (9) p-methoxystyrene, (10) p-chlorostyrene, (11) m-chlorostyrene, (12) diethylstyrene.

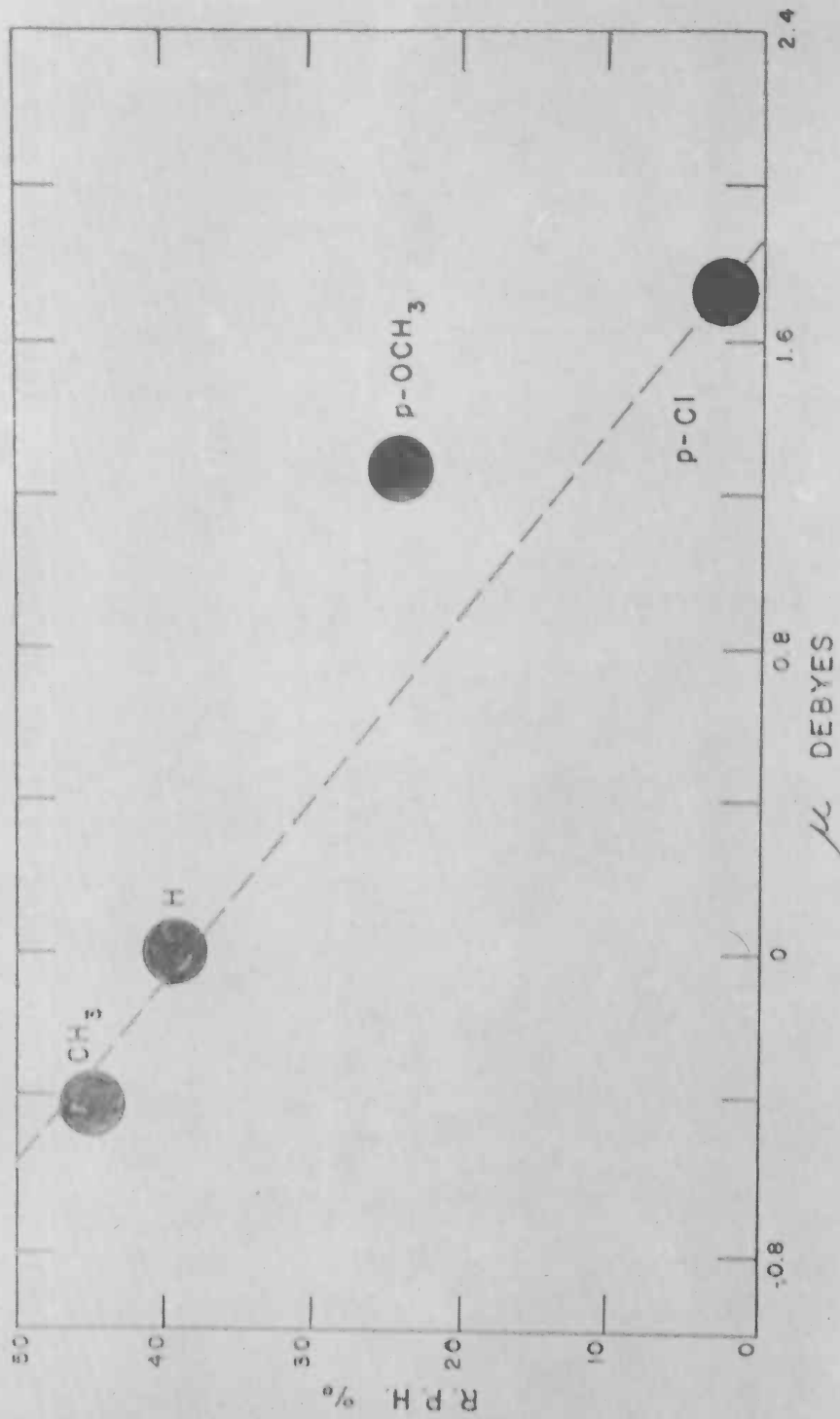
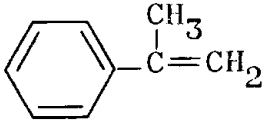
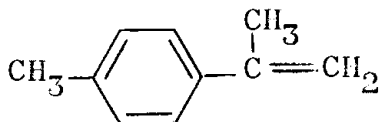
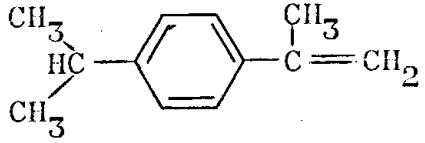


Figure 3. Pulse heights of monosubstituted styrene plastic scintillators versus dipole moments (μ).

The values of the relative pulse height (β -radiation) for a series of plastic scintillators based on substituted α -methyl styrenes are listed in Table 2.

TABLE 2. RELATIVE PULSE HEIGHT VALUES (β -RADIATION) FOR A SERIES OF SUBSTITUTED α -METHYL STYRENES

Structural Formula	R.P.H.* \pm 2
 <p>α-Methyl styrene</p>	5
 <p>p-Methyl-α-methyl styrene</p>	6
 <p>p-Isopropyl-α-methyl styrene</p>	3

*These values were obtained by extrapolation of copolymer data (see reference 1).

B. The Effect of Fluor Structure.

Two series of polyvinyltoluene scintillators were prepared, one of which contained various substituted naphthalenes and the other various substituted biphenyls as the fluor. The relative pulse heights (β -radiation) are listed in Table 3 and are plotted against ϕ in Figure 4.

TABLE 3. RELATIVE PULSE HEIGHTS (β -RADIATION) OF POLY-VINYL TOLUENE SCINTILLATORS CONTAINING (A) SUBSTITUTED NAPHTHALENES AND (B) SUBSTITUTED BIPHENYLS AS THE FLUOR.*

(A) Naphthalene Substituent	No. in Fig. 4	R.P.H. \pm 2
none	1	19
1-methyl	2	13
mixed dimethyl**	3	14
1-methoxy	4	23
1-cyano	5	14
(B) Biphenyl Substituent		
none	6	18
4-phenoxy	7	17
4-cyano	8	25

*All samples contain 0.05% POPOP.

**This material was obtained from the Eastman Organic Chemical Co. and the distilled fraction that was used had the following physical constants: b.p.₁ 93° n_D28° 1.6040.

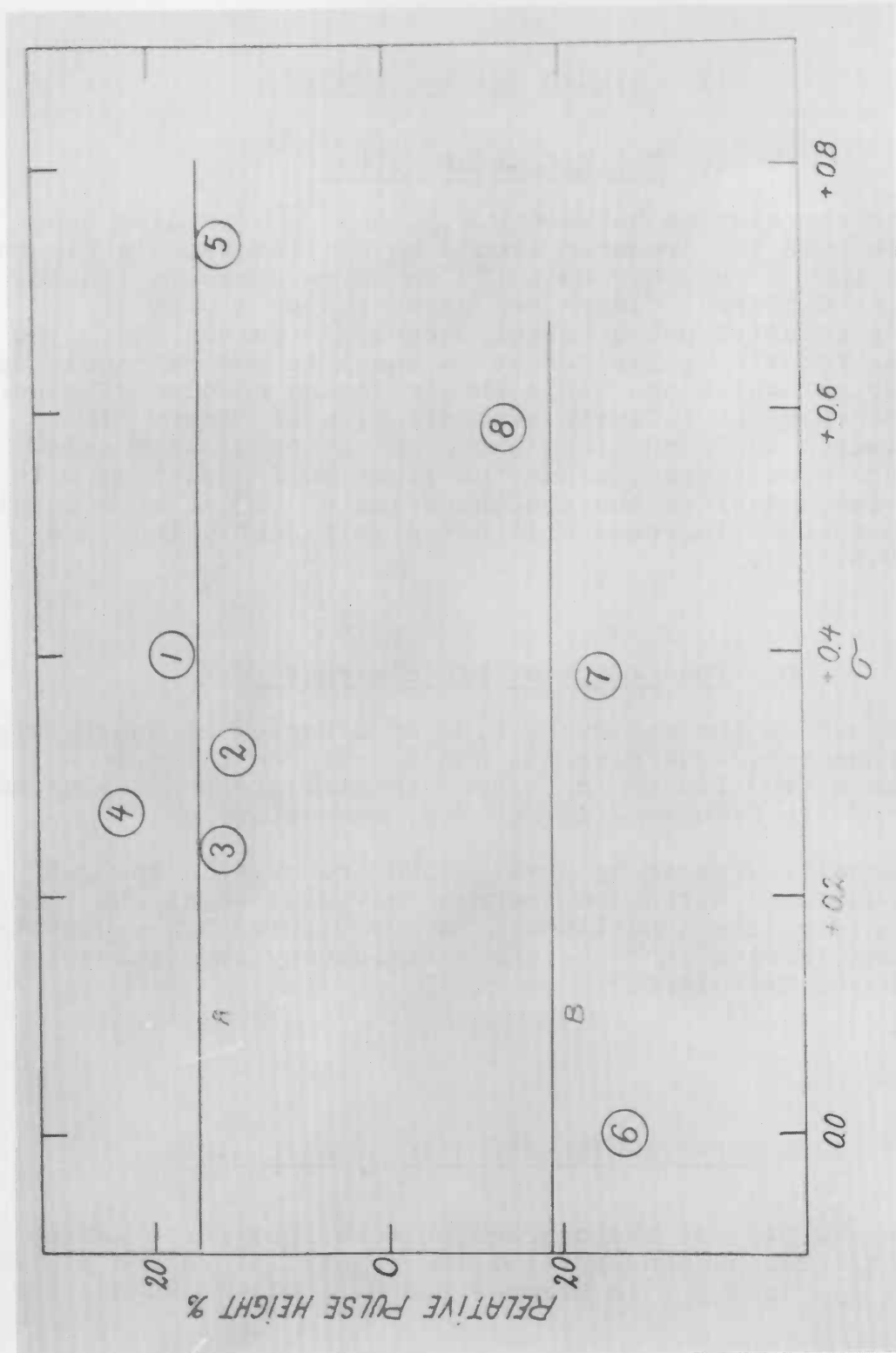


Figure 4. Pulse heights of polyvinyltoluene scintillators containing (A) substituted naphthalene, and (B) substituted biphenyls versus $\bar{\sigma}$.

II. LIQUID SCINTILLATORS.

A. The Effect of Solvent

The correlation between R.P.H. and σ has also been found to hold for aromatic liquid scintillators. In Figures 5 and 6 the γ response data (7) on seven aromatic liquids with nine different fluors are presented as a plot of limiting relative pulse height versus σ values (1). The limiting relative pulse height is equal to the extrapolated pulse height which one would obtain in the absence of fluor self-quenching at infinite concentration of fluor. This approximates the conditions under which the plastic scintillators were tested, since the fluor self-quenching with PTP is low and since the concentration of PTP is at a level where a further increase will not significantly increase the R.P.H. (8).

B. The Effect of Fluor Structure

Values of the maximum R.P.H. of a series of substituted 2,5-diphenyl-1,3-oxazoles (9) and 2,5-diphenyl-1,3,4-oxadiazole (10) fluors in toluene scintillators are plotted versus σ in Figures 7(A) and 7(B) respectively.

Recently a paper by Shvaika and Grekov (11) has come to the authors' attention wherein they also point out that electron donating substituents in substituted 2,5-diphenyl-1,3,4-oxadiazoles increase their efficiency as solutes in toluene scintillators.

III. CRYSTALLINE AROMATIC SCINTILLATORS

Values (12) of the average pulse height for a series of substituted benzene crystalline scintillators are plotted against σ and σ_I in Figures 8 and 9. It is suggested

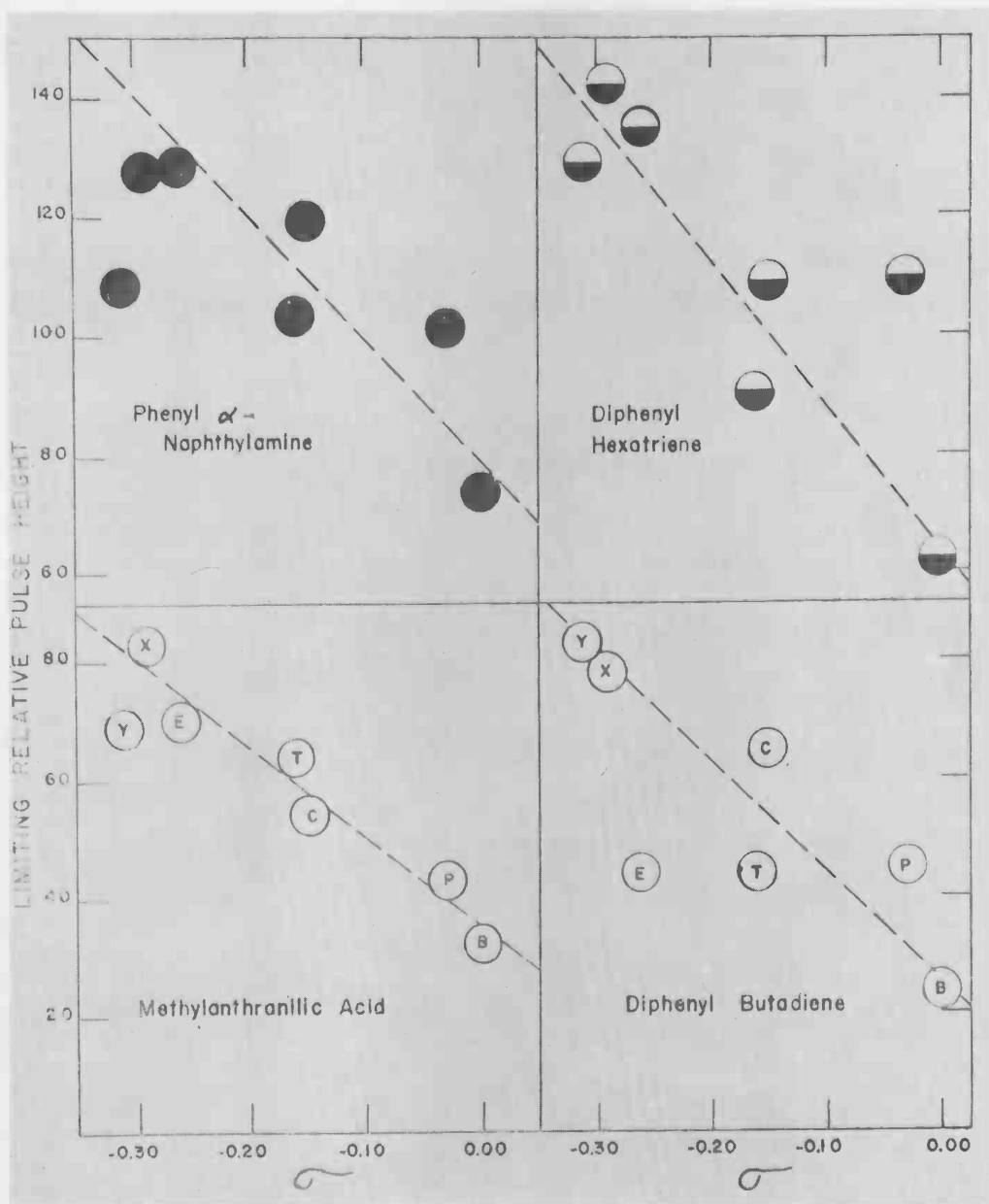


Fig. 5. Limiting relative pulse height versus σ for the indicated solutes in the following solvents: (B) benzene, (P) phenylether, (C) cumene, (T) toluene, (X) xylene, (Y) p-cymene, (E) phenetole.

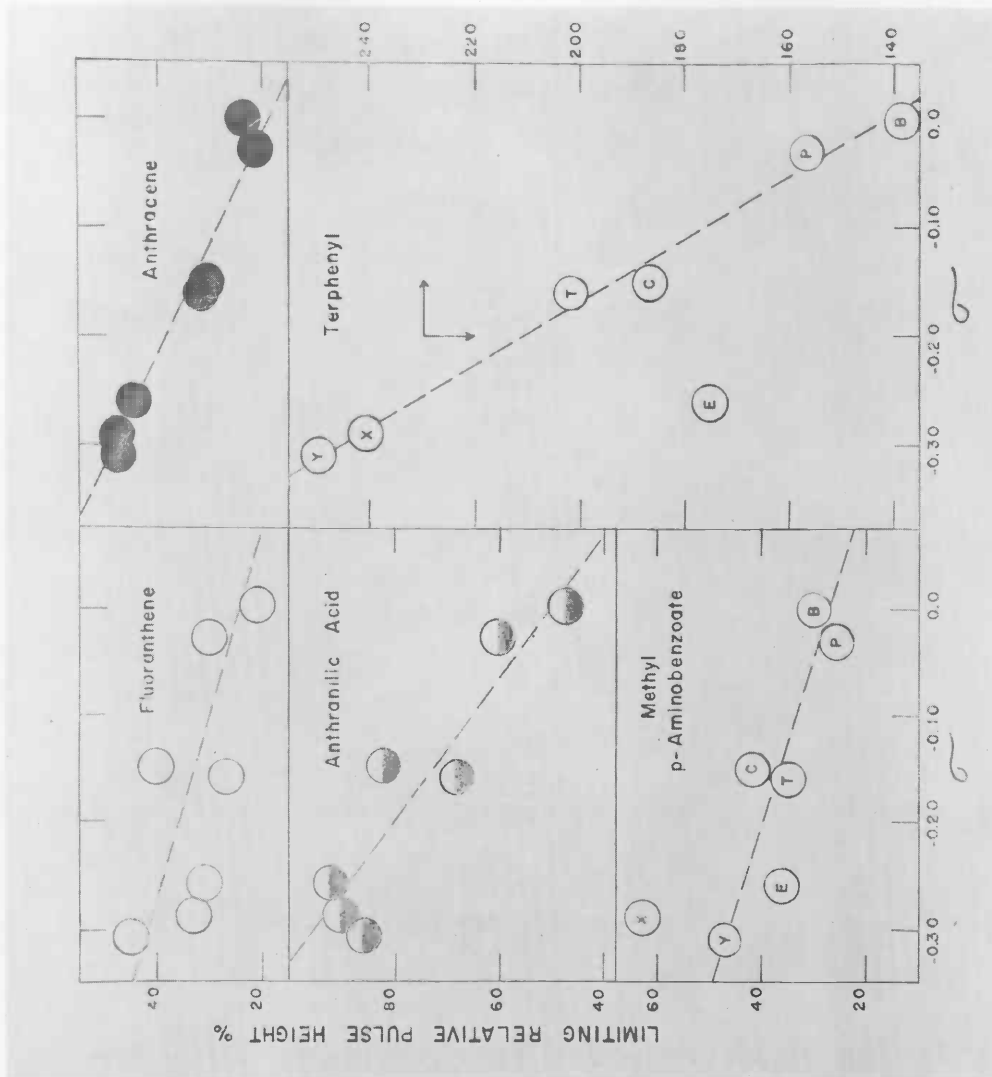


Figure 6. Limiting relative pulse height versus O for the indicated solutes in the following solvents: (B) benzene, (P) phenylether, (C) cumene, (T) toluene, (X) xylene, (Y) p-cymene, (E) phenetole.

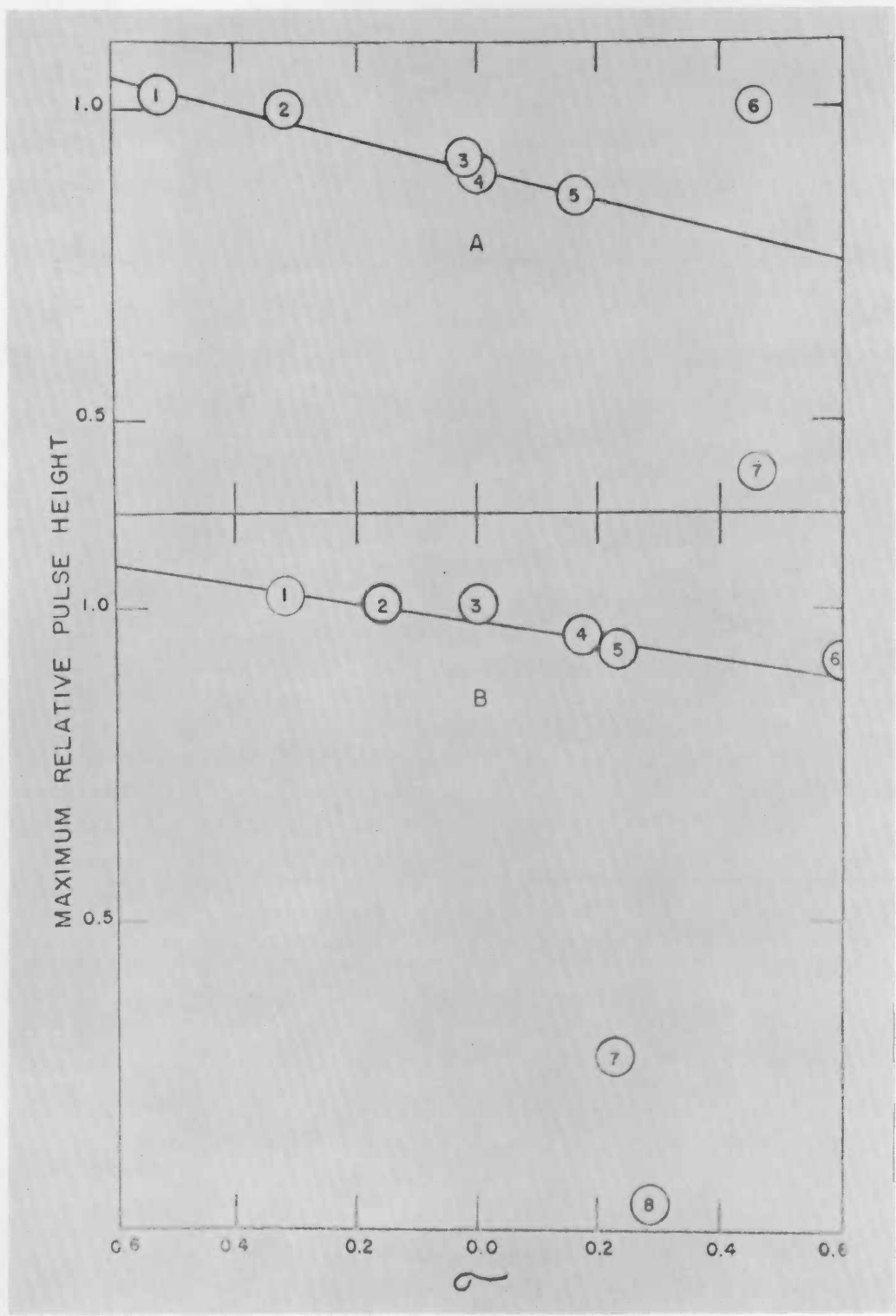


Figure 7. Maximum relative pulse height versus σ for (A) substituted 2,5-diphenyl-1,3,4-oxadiazoles, and (B) 2,5-diphenyl-1,3-oxazoles in toluene.

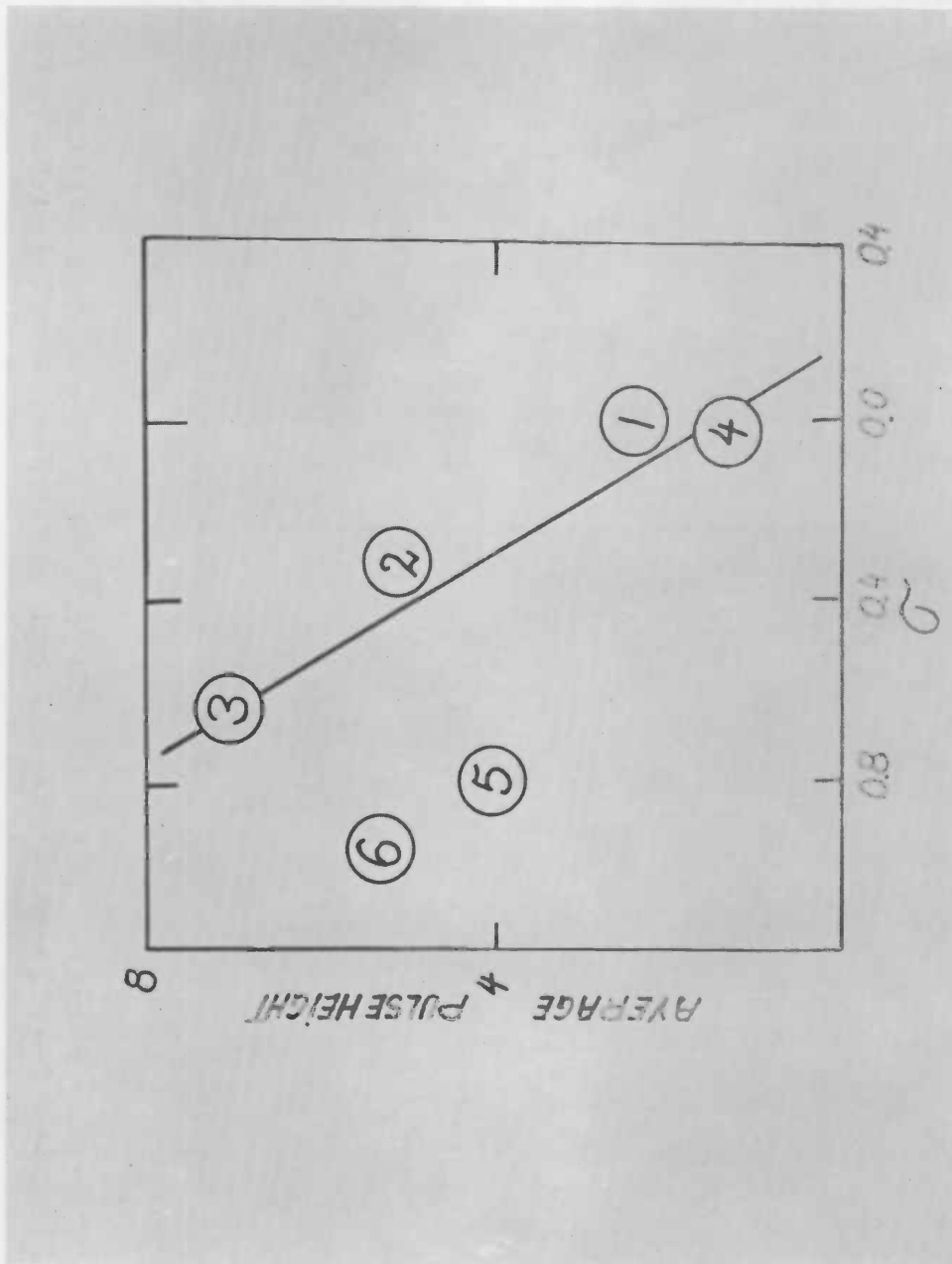


Figure 8. Average pulse height versus σ for crystalline substituted benzene compounds. (1) Benzene, (2) p-cymene, (3) 1,2,4,5-tetramethylbenzene, (4) phenylether, (5) pentamethylbenzene, (6) hexamethylbenzene.

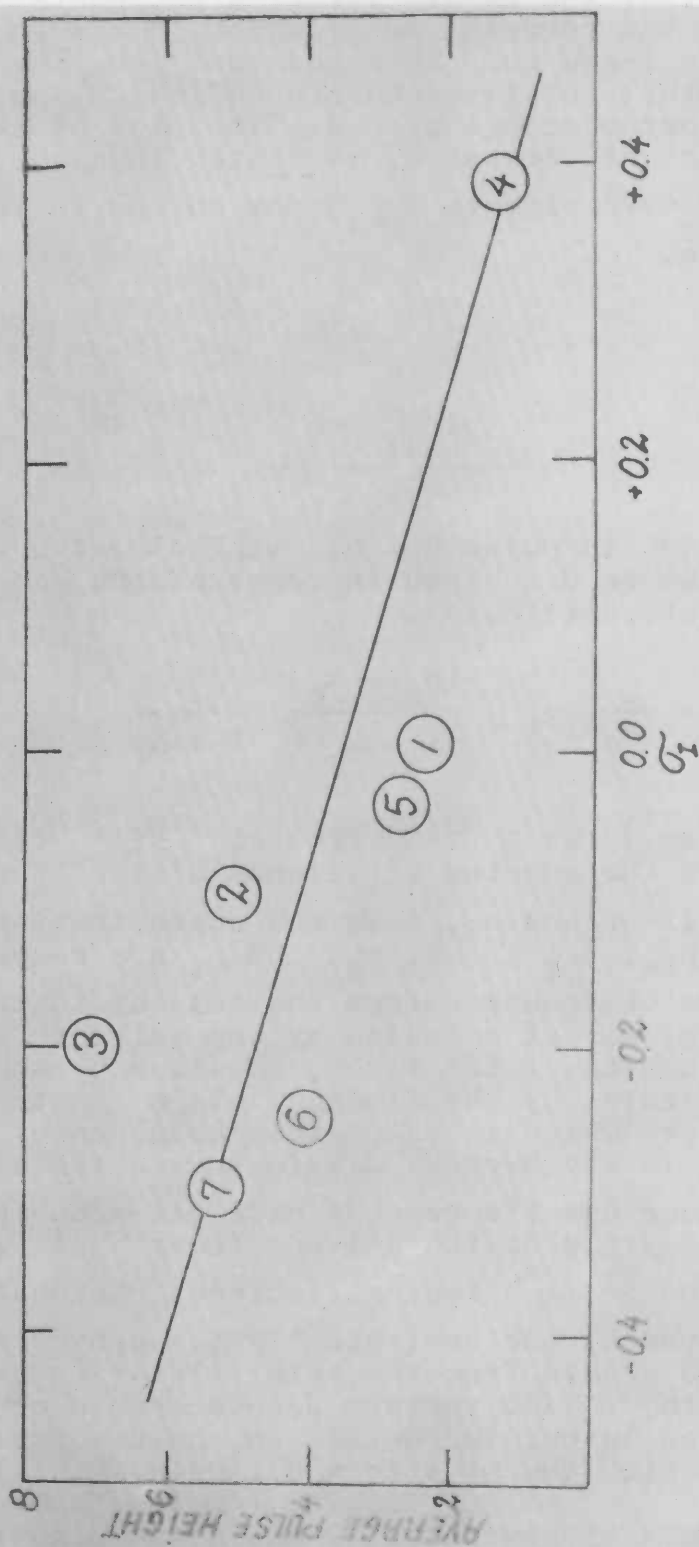


Figure 9. Average pulse height versus σ_I^2 for crystalline substituted benzene compounds. (1) Benzene, (2) p-cymene, (3) 1,2,4,5-tetramethylbenzene, (4) phenylether, (5) diphenylmethane, (6) pentamethylbenzene, (7) hexamethylbenzene.

that the reason that the points for hexa and penta methyl benzene fall off the correlation line for σ is due to steric effects in these compounds and that the σ values for meta and para methyl substituents are no longer applicable when applied to ortho methyl groups. The plot of average relative pulse height versus σ_I is better than the σ plot because the inductive effects (σ_I) may not be influenced by steric effects.

DISCUSSION

The variation in pulse height with solvent and fluor structure can best be discussed in terms of the general pulse height equation (1,8,13).

$$P.H. = \frac{E}{w_o} q_f \sigma \frac{(q_o + k_c)}{1 + k_c} \frac{1}{1 + mc} \quad (1)$$

where $k_c = p_t/(p_{ss} + p_{es})$, $mc = p_{ff}/(p_{ef} + p_i)$, $q_f = p_{ef}/(p_{ef} + p_i)$ is the quantum efficiency of the fluor exclusive of fluor self-quenching, c is the concentration of the fluor, p_t , p_{ss} , p_{es} , $p_{ff} = \beta c$, p_{ef} and p_i are respectively, the probabilities of transfer from the solvent to the fluor, solvent quenching, direct emission by the solvent (very small), self quenching of the fluor, emission by the fluor and internal quenching by the fluor, β is a constant, E is the particle energy which is completely absorbed by the scintillator, w_o is the average dissipated particle energy required to produce one fluorescent excitation in the solvent, q_o is the quantum yield of the solvent (very small in comparison to k_c) and σ is a factor (includes photocathode efficiency, instrument factors, etc.) which converts the number of emitted quanta from the scintillator to an observed pulse height voltage. The various parameters in equation (1) will be considered in greater detail in the discussion of results obtained with the plastic and liquid scintillators.

From the data of Figures 1, 2 and 3 for plastic scintillators and Figures 5 and 6 for liquid scintillators it is

seen that there is an approximate linear correlation between the pulse height and \bar{C} or \bar{C}_I . For the liquid and plastic scintillators since fluor self quenching is unimportant and therefore the pulse height is equal to $E/w_0 q_f$ or stated mathematically $(q_0 + kc)/(1 + kc) = 1$. Since in both cases the fluor was constant for a given series of solvents, it is suggested that the variation in pulse height can be accounted for by a variation in w_0 , the dissipated average particle energy required to produce one fluorescent excitation in the solvent, and/or $q_f = p_{ef}/(p_{ef} + p_i)$ the fluorescent quantum yield of the fluor exclusive of fluor self quenching.

It is postulated here that by varying the solvent the major change in the pulse height arises from a change in the absorption process as characterized by w_0 . With the rather great changes in fluor structure for the liquid scintillators it seems unlikely that the interactions between each fluor with each solvent would be the same as indicated by the similarity of slope in the \bar{C} correlations unless the probability of internal quenching p_i was small.

It was of further interest to determine something about the locus of absorption of energy in the plastic solvent molecule.

Substitution of a methyl group for the α -hydrogen in polystyrene to give poly- α -methyl styrene, reduced the R.P.H. from 39 to 5 (Table 2). On the other hand it has been shown that substitution of a methyl group in the ring caused an increase in R.P.H. On this basis, it might be expected that substitution of a methyl group in the ring of poly- α -methyl-styrene would increase its R.P.H., but the data in Table 2 show that the expected increase was not obtained. These results suggest that the α -hydrogen is a preferred locus of energy absorption. Furthermore, it appears that the α -hydrogen must be in the backbone of the polystyrene chain since the R.P.H. (Table 1) of *p*-isopropyl styrene which has two α -hydrogens was no greater than that obtained with methyl styrene. The primary absorption process in liquid organic scintillators would appear to be different from that in plastic scintillators, since many aromatic solvents which have good scintillation properties do not have an α -hydrogen of the type discussed here, e.g., benzene and other solvents in Figures 5 and 6.

The role of the substituents with negative σ_I values in enhancing the R.P.H. values may, however, be similar in both liquids and plastics.

When the solvent type was kept constant and the aromatic substituents of the fluor were varied a σ versus maximum relative pulse height correlation was also obtained for solutes in plastic and liquid scintillators (Figures 4 and 7). A comparison of the slopes of the line of Figures 1, 2, 5 and 6 with Figures 4, 7 shows that the pulse height varies much more with a change in the σ value of the solvent than with an equal change in the σ value of the fluor. The variation of pulse heights in Figures 4 and 7 can be attributed on the basis of equation (1) to a change in p_t , w_o or q_f . Since the solvent composition is fixed it is reasonable to assume, on the basis of the previous discussion, that w_o does not account for the variation in pulse heights. From the data it is presently not possible to distinguish whether changes in q_f or p_t are responsible for changes in the observed pulse height.

It is interesting to note that aromatic crystalline scintillators also gave a R.P.H. versus σ correlation such that the pulse height increased with an increase in the electronegativity of the substituents on the benzene ring. In this case no fluor was present thus the absorption and transfer step may both depend on the electron donating power of the substituents.

In summary, an overall scintillation mechanism for plastic, liquid and crystalline scintillators which would be in harmony with the present observation requires first, an absorption of a fraction of the dissipated particle energy by the solvent and secondly, a transfer of the energy to the fluor molecule. The presence of nuclear substituents donating electrons to the benzene conjugated system probably facilitate the primary absorption process. The transfer of energy from the excited solvent molecules to the fluor molecules may, however, be facilitated by a favorable electron density distribution between the two.

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