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## GAS CHROMATOGRAPHIC, SPECTROPHOTOMETRIC AND ELECTRO-CHEMICAL BEHAVIOUR OF SUBSTITUTED *s*-TRIAZINES

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### SUMMARY

The behaviour of 18 *s*-triazine herbicides was studied gas chromatographically, spectrophotometrically and electrochemically. The retention indices were measured on three stationary phases, Carbowax 20M, Versamid 900 and an SE-30 + Reoplex 400 mixed phase, and the effect of the substituents in the 2-, 4- and 6-positions on the retention data is discussed. The differences in the retention indices on two phases,  $\Delta I$ , were correlated with the basicities and the dipole moments of the substances studied. The UV spectra of the *s*-triazines were measured in methanol. A study of the anodic electrochemical behaviour of these substances was carried out in anhydrous acetonitrile. The  $E_{1/2}$  values obtained indicated that the substances strongly resisted oxidation and the results are discussed together with the gas chromatographic and spectrophotometric data in relation to the structures of the *s*-triazines.

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### INTRODUCTION

*s*-Triazines are widely used as herbicides in agriculture and industry. They affect primarily the roots of plants and destroy most weeds. Some of these substances, in addition to being important herbicides, exhibit fungicidal properties or are used as pharmaceuticals.

The *s*-triazine herbicides were first synthesized by Geigy, by substituting 1,3,5-triazine (*s*-triazine) in the 2-, 4- and 6-positions. The *s*-triazine character is determined by the substituent in the 2-position, generally chlorine (the commercial name ends with -azine), methoxy (ending -tone) and thiomethyl (ending -tryne). The 4- and 6-positions are usually substituted with various aminoalkyl groups.

The herbicidal effect of *s*-triazines depends on the nature of the substituent in the 2-position and on the number of carbon atoms in the aminoalkyl groups in the 4- and 6-positions; the effectiveness decreases with an increase in the number of carbon atoms. The selective effects of these substances can be varied by replacing Cl with  $\text{OCH}_3$  or  $\text{SCH}_3$ .

The *s*-triazines have been analyzed spectrophotometrically in the visible and UV regions and by paper (PC) and thin-layer chromatography (TLC)<sup>1</sup>. The spectral methods are sufficiently sensitive but are lacking in separation possibilities. PC and

TLC permit separations, but yield only semi-quantitative results. The shortcomings of the above methods are overcome by using gas chromatography (GC), which can be used both for the determination of the purity of the preparations<sup>2,3</sup> and for the analysis of residues<sup>3-11</sup>. Polar stationary phases, possibly combined with non-polar phases, are most often employed for separations of *s*-triazines. The support must be inert, because of the polar character of the *s*-triazines. Triazines can be detected with a flame-ionization detector, as well with specific detectors, e.g., coulometric<sup>4,6</sup>, flame-photometric<sup>4,12</sup>, Coulson electrolytic conductance<sup>4,6,8-10,13,14</sup> and thermionic<sup>13</sup> detectors.

In view of the importance of these substances, studies of their properties and the development of sensitive methods for their determination are required. Most papers published so far have been concerned with applications and deal with the determination of one or several components in soil, water or grain. A systematic study of the basic properties of *s*-triazine herbicides is lacking, and was attempted in this work, in which the GC, spectrophotometric and electrochemical behaviour of variously substituted *s*-triazines was studied.

## EXPERIMENTAL

### Methods

GC measurements were carried out isothermally on a Hewlett-Packard 5700 A instrument with a flame-ionization detector. Metal columns (140 cm × 3 mm I.D.) were used. The temperatures of the column were 195° and 215° and those of the injection block and the detector were 230° and 210°, respectively. Nitrogen was used as the carrier gas at a flow-rate of 40 ml/min. The columns were packed with 3% (w/w) Carbowax 20M on Chromosorb W (silanized, 60-80 mesh), 5% Versamid 900 on Chromosorb W (60-80 mesh) and a mixed phase of 5% SE-30 + 2% Reoplex 400 on Chromaton N-ÅW (60-80 mesh).

Spectrophotometric measurements were performed on a Unicam SP-800 instrument with 1-cm quartz cuvettes in absolute methanol at 20°, at concentrations of 10<sup>-6</sup>-10<sup>-4</sup> M.

Electrochemical measurements were carried out in a 0.1 M sodium perchlorate solution in anhydrous acetonitrile using a platinum rotating disk indicator and saturated calomel reference electrodes (S.C.E.). A detailed description of the apparatus and the measurements has been given elsewhere<sup>15</sup>.

### Materials

All test *s*-triazines were products of Geigy, Basle, Switzerland. The substances were purified by multiple recrystallization from methanol and then their purity was checked by determination of the melting points, elemental analysis and GC.

Methanol (spectrally pure, Lachema, Brno, Czechoslovakia) was purified by the procedure described by Smisko and Dawson<sup>16</sup>. Acetonitrile (p.a. grade, Merck, Darmstadt, G.F.R.) was purified by the procedure described earlier<sup>15</sup>. The *n*-alkanes used in the calculation of the retention indices were obtained from the Applied Science Labs., State College, Pa., U.S.A.

SE-30 and Carbowax 20M were products from Carlo Erba, Milan, Italy,

Reoplex 400 and Versamid 900 were obtained from Hewlett-Packard, Avondale, Pa., U.S.A., Chromaton N-AW (60–80 mesh) was supplied by Lachema and Chromosorb W (silanized, 60–80 mesh) by Carlo Erba.

## RESULTS AND DISCUSSION

### Gas chromatographic behaviour

Carbowax 20M, Versamid 900 and Reoplex 400 + SE-30 were selected as stationary phases for the study of the effect of the structures of *s*-triazines on their GC behaviour. McReynolds indices for these phases (see Table I) indicated that Carbowax 20M will most strongly retain acidic substances (nitropropane). Reoplex 400 + SE-30 and Versamid 900 retain acidic and basic substances approximately equally. The non-selective character of these phases was also verified by the linear dependence of  $\log p_0$  ( $p_0$  = saturated vapour pressure) on the retention indices (Fig. 1).

TABLE I

McREYNOLDS CONSTANTS

Stationary phase	$\Sigma\Delta I^*$	Benzene	Butanol	2-Pentanone	Nitropropane	Pyridine	2-Methylpentanol	Iodobenzene
SE-30 + Reoplex 400 (5:2)	940	115	214	160	230	221	196	93
Versamid 900	969	108	309	137	208	207	222	110
Carbowax 20M	2308	322	536	368	572	510	387	282

$$* \Sigma\Delta I = \Delta I_{\text{benzene}} + \Delta I_{\text{butanol}} + \Delta I_{\text{2-pentanone}} + \Delta I_{\text{nitropropane}} + \Delta I_{\text{pyridine}}$$

The retention indices of the *s*-triazines were measured at 195° and 215° on the three stationary phases<sup>17</sup> and the results are given in Table II. An example of the separation of a mixture of *s*-triazines on Carbowax 20M is shown in Fig. 2.

All of the stationary phases tested are suitable for the separation of *s*-triazines. Compared with Carbowax 20M, the retention indices on Versamid 900 and Reoplex 400 + SE-30 are 300–400 and 600–700 units lower, respectively, so that lower experimental temperatures can be used.

The retention data for the *s*-triazines depend primarily on the nature of the substituent in the 2-position. Methoxy-*s*-triazines are eluted first, then chloro derivatives and finally thiomethyl-*s*-triazines.

In the series of chloro-*s*-triazines, the order of retention depends chiefly on the spatial shielding of the –NH groups in the 4- and 6-positions by alkyl groups and on their number. The lowest retention index on Versamid 900 is exhibited by chlorazine [2-chloro-4,6-bis(diethylamino)-*s*-triazine] (the value, 2021, was calculated from the data given by Henkel and Ebing<sup>18</sup>), which contains only *tert*-amino groups. It is followed by trietazine, propazine, terbutylazine, atrazine and simazine. The *tert*-butyl group gives rise to greater spatial shielding than the isopropyl group and the weakest shielding is caused by ethyl groups. For this reason simazine is eluted last. A similar dependence can also be observed in the series of methoxy- and thiomethyl-*s*-triazines.

The difference in the retention indices on Carbowax 20M and Reoplex 400 +

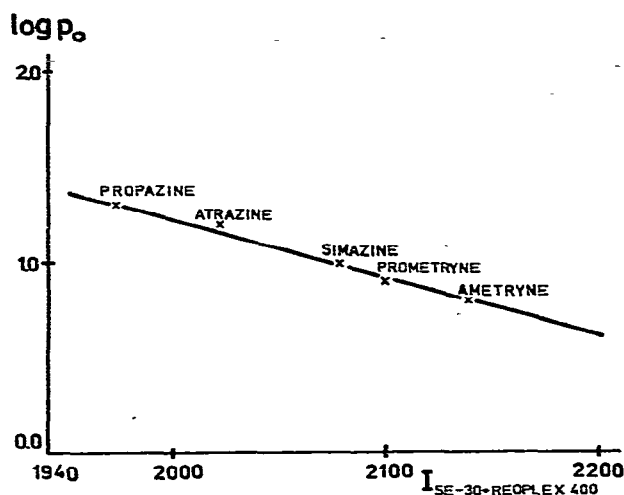


Fig. 1. Dependence of  $\log p_0$  on retention indices of *s*-triazines.

SE-30,  $\Delta I$ , depends on the nature of the substituent in the 2-position and also on the number and kind of alkyl groups bound to the amino groups in the 4- and 6-positions. *s*-Triazines have acid-base properties. In acidic media, the neutral form is converted into the protonated form. The dissociation constant is most strongly affected by the substituent in the 2-position. It follows from the comparison of the chemical properties that the basicity of these substances increases with substituents in the 2-position in

TABLE II  
RETENTION INDICES OF 18 *s*-TRIAZINES ON THREE STATIONARY PHASES

Common name	2-Substituent	4-Substituent	6-Substituent	Mol.wt.	$I_A^*$	$I_B^*$	$I_C^*$	$\Delta I_{A-C}$	$\Delta I_{A-B}$
—	Cl	NH <sub>2</sub>	NHtBu	201.5	2336	—	1766	570	—
Ipazine	Cl	N(Et) <sub>2</sub>	NHiPr	243.6	2461	2142	1907	554	319
—	Cl	NHtBu	NHtBu	257.8	2501	2185	1938	563	316
Trietazine	Cl	NHEt	N(Et) <sub>2</sub>	229.7	2557	2196	1932	625	361
Propazine	Cl	NHiPr	NHiPr	229.7	2633	2262	1973	660	371
Terbutylazine	Cl	NHEt	NHtBu	229.7	2664	2288	1999	665	376
Atrazine	Cl	NHEt	NHiPr	215.7	2722	2318	2023	699	404
Simazine	Cl	NHEt	NHEt	201.5	2806	2375	2078	728	431
Prometone	OCH <sub>3</sub>	NHiPr	NHiPr	225.3	2539	2199	1916	623	340
Terbutone	OCH <sub>3</sub>	NHtBu	NHEt	225.3	2570	2205	1938	632	365
sec.-Bumetone	OCH <sub>3</sub>	NHEt	NHsecBu	225.3	2676	2302	2015	662	374
Simetone	OCH <sub>3</sub>	NHEt	NHEt	197.2	2680	2270	1990	690	410
Prometryne	SCH <sub>3</sub>	NHiPr	NHiPr	241.3	2758	2378	2099	659	380
Terbutryne	SCH <sub>3</sub>	NHEt	NHtBu	241.3	2793	2403	2122	671	390
Ametryne	SCH <sub>3</sub>	NHEt	NHiPr	227.3	2837	2418	2139	698	419
Desmetryne	SCH <sub>3</sub>	NHMe	NHiPr	213.3	2868	2452	2141	727	416
Simetryne	SCH <sub>3</sub>	NHEt	NHEt	213.3	2915	2465	2185	730	450
Metoprotryne	SCH <sub>3</sub>	NHiPr	NH(CH <sub>2</sub> ) <sub>5</sub> - OMe	271.4	3202	2726	2457	745	476

\* A = Carbowax 20M (215°); B = Versamid 900 (195°); C = SE-30 + Reoplex 400 (195°).

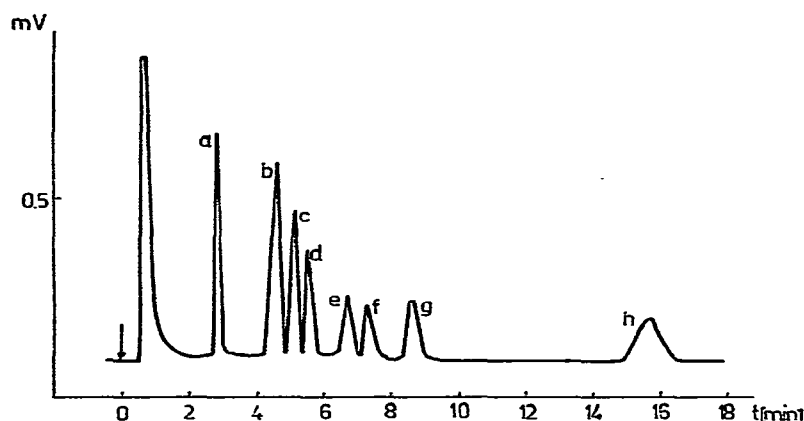


Fig. 2. Separation of *s*-triazines on Carbowax 20M at 215°. (a) 2-Chloro-4-amino-6-*tert.*-butylamino-*s*-triazine; (b) 2-chloro-4,6-bis(*tert.*-butylamino)-*s*-triazine; (c) prometon; (d) terbutone; (e) propazine; (f) terbutylazine; (g) atrazine; (h) simetryne.

the order  $\text{Cl} < \text{SCH}_3 < \text{OCH}_3 < \text{OH}$ . These properties are also reflected in the GC behaviour; the highest  $\Delta I$  values were obtained for the weakest bases, *i.e.*, the strongest conjugated acids.

The properties of related *s*-triazines are compared in Table V, from which some other dependences can be derived. In the series of chlorotriazines (propazine, atrazine and simazine), the difference in retention indices on Carbowax 20M and Reoplex 400 + SE-30 is proportional to  $\text{p}K_{\text{B}}$ . The dipole moment also has an effect on the retention indices.

The dependence of the retention indices on the two stationary phases can be used for identification purposes. As can be seen in Fig. 3, the individual groups of *s*-triazines lie on different straight lines.

#### Spectrophotometric behaviour

Although the triazine herbicides are much more soluble in methanol than in water, no systematic study of their UV spectra in methanol has been carried out. Therefore, we measured the UV spectra of 18 commercial *s*-triazine herbicides, determining  $\lambda_{\text{max}}$  and the molar absorptivity,  $\epsilon$ . These data are given in Table III.

In contrast to the spectra in aqueous solutions, where all *s*-triazines exhibit two absorption maxima<sup>19</sup>, methoxy- and thiomethyl-*s*-triazines have only a single maximum between 219 and 230 nm, with  $\epsilon_1 \approx 10^4$ . Chloro-*s*-triazines have one more maximum from 263 to 270 nm, with  $\epsilon_2 \approx 10^3$  (Table III).

The spectra of atrazine, atratone and ametryne are shown in Fig. 4; the spectra of the other chloro-, methoxy- and thiomethyl-*s*-triazines differ only in the maximum position and  $\epsilon$ , but the character of the spectra remains the same.

As can be seen from Table III, the differences in the  $\lambda_{\text{max}}$  and  $\epsilon$  values are small and cannot be used for characterization of these herbicides. Only chloro-*s*-triazines can be differentiated, on the basis of the occurrence of the second maximum.

Similar to the gas chromatographic data, replacement of H in the  $-\text{NH}$  groups

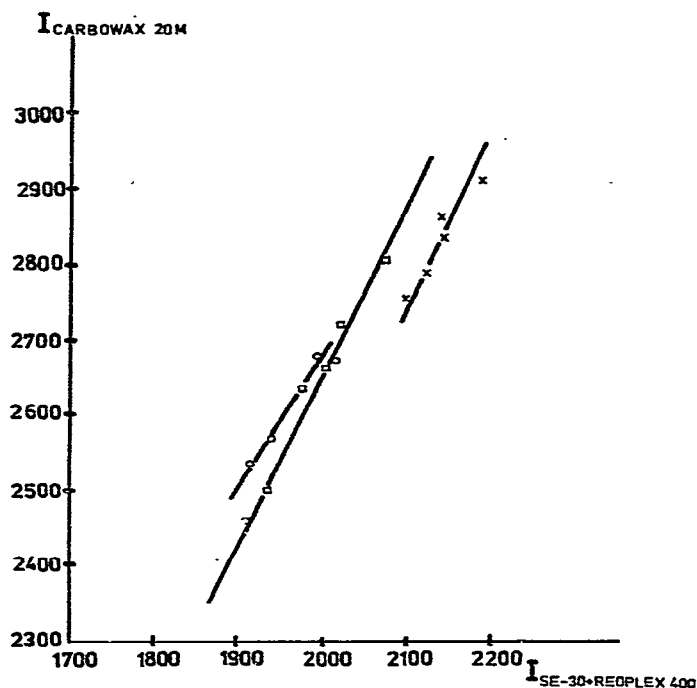


Fig. 3. Dependence of  $I_{\text{Carbowax 20M}}$  on  $I_{\text{SE-30+ Reoplex 400}}$  for chloro-*s*-triazines (□), methoxy-*s*-triazines (○) and thiomethyl-*s*-triazines (×).

TABLE III

ABSORPTION MAXIMA AND MOLAR ABSORPTIVITY OF 18 *s*-TRIAZINES

<i>s</i> -Triazine	$\lambda_1$ (nm)	$\epsilon_1^*$ ( $l \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ )	$\lambda_2$ (nm)	$\epsilon_2^{**}$ ( $l \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ )
2-Chloro-4-amino-6- <i>tert.</i> -butylamino- <i>s</i> -triazine	231	12000	Broad maximum	
2-Chloro-4,6-bis( <i>tert.</i> -butylamino)- <i>s</i> -triazine	223	36000	264	3300
Trietazine	227	44300	267	4300
Propazine	222	32000	268	3100
Terbutylazine	223	19500	263	1800
Atrazine	222	41000	263	3900
Simazine	222	36000	263	3100
Ipazine	227	43100	266	4300
Prometone	219	40200	—	—
Terbutone	219	33600	—	—
Simetone	222	38300	—	—
Prometryne	223	42000	—	—
Terbutryne	223	21200	—	—
Ametryne	222	40000	—	—
Desmetryne	221	33700	—	—
Simetryne	222	44400	—	—

\* For the concentration range  $10^{-5}$ – $10^{-3}$  M.

\*\* For the concentration range  $10^{-5}$ – $10^{-4}$  M.

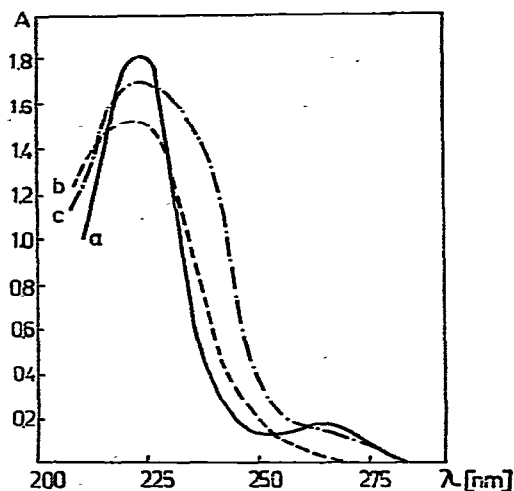


Fig. 4. Absorption spectra of atrazine (a), atratone (b) and ametryne (c) ( $5 \cdot 10^{-5}$  M solution in methanol).

with alkyl groups affects the spectrophotometric properties of *s*-triazines. An increase in the number of alkyl groups leads to a bathochromic shift; this can be demonstrated by comparing the  $\lambda_{\max}$  values of simazine and trietazine or atrazine and ipazine (see Table III). The lengths of the alkyl chains in the 4- and 6-positions do not substantially affect the  $\lambda_{\max}$  values.

#### *Electrochemical behaviour*

Data on the electrochemical oxidation of *s*-triazines are lacking in the literature. As these substances are very resistant, studies were carried out in anhydrous acetonitrile, which permits electrochemical oxidations of such substances. Moreover, hydrolysis and other interfering effects do not occur in the anhydrous medium and consequently the results are easier to interpret in relation to the structure of the test substances.

The *s*-triazines yielded a single anodic wave on a platinum rotating disk electrode in a 0.1 M anhydrous acetonitrile solution of sodium perchlorate<sup>20</sup> (see Table IV).

It follows from Table IV that chloro-*s*-triazines have the highest  $E_{1/2}$  values in the series of the chloro, methoxy and thiomethyl derivatives. The differences in the  $E_{1/2}$  values for the methoxy and thiomethyl derivatives are small.

In the series of chloro-*s*-triazines, the  $E_{1/2}$  values depend on the number of alkyl groups per amino group in the 4- and 6-positions, similar to the spectrophotometric and GC data. Replacement of hydrogen atoms with alkyl groups leads to a considerable decrease in  $E_{1/2}$  (simazine with respect to trietazine, atrazine with respect to ipazine). On the other hand, the length of the alkyl group has no perceptible effect on the  $E_{1/2}$  values.

As the *s*-triazine proper is not oxidized (see Table IV), the exocyclic amino groups in the 4- and 6-positions act as electron donors. The presence of an electro-

TABLE IV  
ANODIC HALF-WAVE POTENTIALS ( $E_{1/2}$ ) OF 17 *s*-TRIAZINES

<i>s</i> -Triazine	$E_{1/2}$ (V vs. S.C.E.)	<i>s</i> -Triazine	$E_{1/2}$ (V vs. S.C.E.)
<i>s</i> -Triazine	Not oxidized	Prometone	1.77
Ipazine	1.77	Terbutone	1.79
2-Chloro-4,6-bis( <i>tert.</i> -butylamino)- <i>s</i> -triazine	2.07	Simetone	1.79
Trietazine	1.77	Prometryne	1.83
Propazine	1.95	Terbutryne	1.78
Terbutylazine	2.01	Ametryne	1.77
Atrazine	2.02	Desmetryne	1.78
Simazine	1.97	Simetryne	1.79

negative atom (Cl) causes a decrease in the electron density on the nitrogen atom (the dipole moment increases, see Table V) and  $E_{1/2}$  increases. Hence *s*-triazines derivatives with a methoxy or thiomethyl group in the 2-position and containing *tert.*-amino groups will be most readily oxidized in anhydrous acetonitrile, *i.e.*, will have the lowest  $E_{1/2}$  values.

The  $E_{1/2}$  values were correlated with the  $pK_B$  values obtained in an aqueous solution<sup>21</sup>, and marked agreement was found; the substances with the highest  $pK_B$ , *i.e.*, the least basic substances, have the highest  $E_{1/2}$  values.

A comparison of the experimental data and some literature values<sup>21</sup> for a series of similar *s*-triazines is given in Table V.

TABLE V  
COMPARISON OF SOME CHARACTERISTICS OF SIMILAR *s*-TRIAZINES

<i>s</i> -Triazine	$I_{carb.}$	$\Delta I$	$E_{1/2}$	$\mu^*$ (ref. 21)	$pK_a$ (refs. 21, 22)
Propazine	2633	660	1.95	4.52	1.85
Prometryne	2758	659	1.83	3.54	4.05
Prometone	2539	623	1.77	2.94	4.28
Atrazine	2722	699	2.02	4.63	1.68
Ametryne	2837	698	1.77	3.15	4.10
Simazine	2806	728	1.97	—	1.65
Simetryne	2915	730	1.79	—	4.04
Simetone	2680	690	1.79	—	4.17
Terbutylazine	2664	665	2.01	—	1.94
Terbutryne	2793	671	1.78	—	4.38
Terbutone	2570	632	1.79	—	4.46

\* $\mu$  = Dipole moment in Debijes.

## CONCLUSION

Individual *s*-triazines can be differentiated chiefly on the basis of the retention indices (Table V). The differences in the retention indices on two stationary phases with different polarities can serve for distinguishing methoxy- from thiomethyl- and



chloro-*s*-triazines, which do not differ significantly. On the other hand, chloro-derivatives can be differentiated from methoxy and thiomethyl derivatives on the basis of the  $E_{1/2}$  values, similar to differentiation on the basis of the  $pK_B$  values. The differences between thiomethyl- and methoxy-*s*-triazines are small. Spectrophotometric data only permit the differentiation of chloro-*s*-triazines on the basis of the occurrence of the second absorption maximum. *s*-Triazines variously substituted in the 2-position differ in their dipole moments, but no general conclusions can be drawn because of the limited number of literature values available.

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