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DIELECTRIC RELAXATION OF SOME NEWLY SYNTHESIZED AROMATIC COMPOUNDS FROM MICROWAVE ABSORPTION MEASUREMENTS

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The dielectric loss ε'' of dilute solutions of five newly synthesized phthalazine derivatives in benzene has been studied in the microwave region between 0.3 and 15 GHz at 20°C. The data have been analysed for two or three absorption regions. The results are interpreted in terms of dipole reorientation by molecular and intermolecular rotation. The activity of these compounds on some fungi was determined and a linear relation was found between this activity and the intramolecular orientation of those compounds.

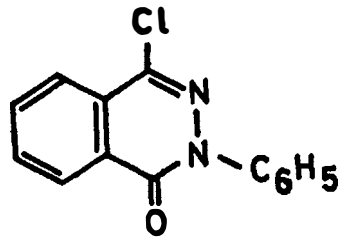
1. Introduction

Many dielectric measurements were carried out on dilute solutions of aromatic molecules in non-polar solvents in order to study the molecular and intramolecular orientations. The aim of this work is to study the dielectric relaxation of five large aromatic molecules in benzene solutions over a wide frequency range. The molecules were prepared in the National Research Center and so no dielectric data for them are yet available. It is also aimed to study the effect of internal mobility of such molecules on their activities.

2. Experimental

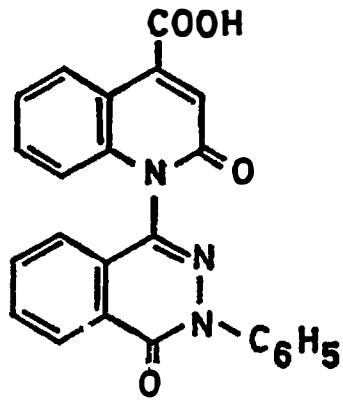
Materials: In this study five newly synthesized phthalazine derivatives (A1——A5) in benzene solutions were used. A solution of 1 : 2 dihydro-4-hydroxy-*1*--*oxo*-*2*-phenyl phthalazine (20 gm) in phosphoryle chloride (20 ml) was refluxed for 4 hours then cooled and poured into 5 N-sodium hydroxide solution (200 ml)

containing crushed ice. After standing for one hour a solid was formed. It was isolated and crystallized from aqueous ethanol to give (A 1) m. p. 130°C.



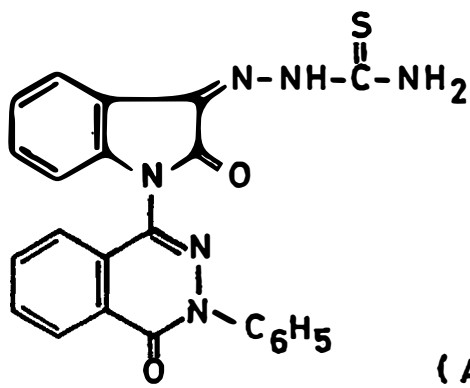
(A 1)

Reaction of isatino phthalazine with malonic acid in glacial actic acid was heated under reflux for 3 hours and recrystallized from cyclohexane to give (A 2) m. p. 73—75°C.



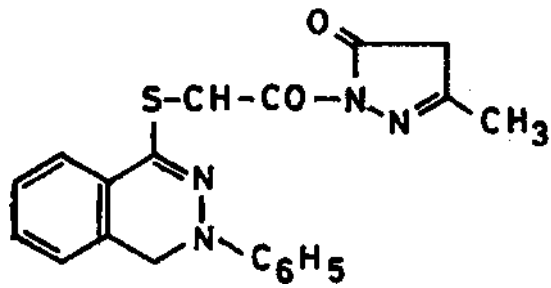
(A 2)

A mixture of isatino phthalazine and of thio-semicarbazide in absolute alcohol was heated under reflux for 6 hours. Recrystallized from cyclohexane to give the isatino compound (A 3) m. p. 93—95°C.



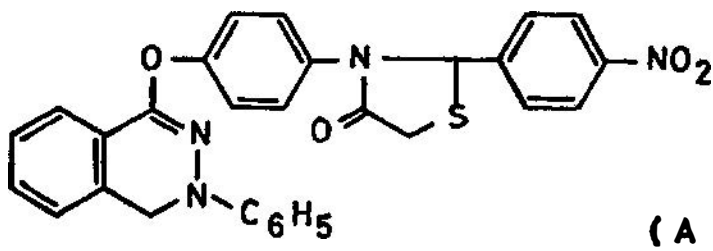
(A 3)

Reaction of 1 : 2-dihydro-1-*oxo*-2-phenyl phthalazine -4- thioactic acid hydrazide with ethyl aceto acetate and absolute alcohol was refluxed for one hour. Recrystallized from methyl alcohol to give pyrazolone-pathalazine derivative (A 4) m. p. 139—141°C.



(A 4)

Reaction of 1 : 2 dihydro-1-*oxo*-2-phenyl phthalazine-4-aldexyde with thio glycolic acid to give (A 5) and recrystallized from acetic acid m. p. 224—225°C.



(A 5)

Benzene "Analar" from BDH was used. It was refluxed over sodium wire and distilled before use.

The biological activity of the mentioned compounds on Asperigllus neiger was determined using the cup-plate agar method[1,2]. The inhibition zone appeared clear to the background which is turbid and opaque due to the thickness of the organism.

Measurements: The dielectric loss ε'' in the frequency range between 0.3 and 15 GHz was measured using the sweep frequency spectrometer established in the National Research Centre, Cairo, similar to that described previously[3]. The accuracy of the measurements amounts to $\pm 3\%$.

The static dielectric constant ε_0 was measured at 2 MHz using the dipolemeter DMO1 from WTW to an accuracy better than 0.5%. The refractive index n_D was measured using an Abbe refractometer, Carl Zeiss, Jena, model G to an accuracy of 10^{-4}. All the measurements were carried out at 20°C using an ultrathermostat.

The measurements of ε_0 and n_D were used to calculate the dipole moment from the equation[4],

$$\mu^2 = \frac{27\,kT}{4\pi L} \cdot \frac{M}{\varrho} \cdot \frac{(\Delta\varepsilon_0 - \Delta n_D^2)/x}{(\varepsilon_L + 2)^2} \qquad (1)$$

where ε_L is the dielectric constant of the solvent, k is Boltzmann's constant, L, s Avogadro's constant, ϱ and M are the density and molecular weight of the solvent, x is the mole fraction, Δ means the difference between solution and solvent and n_D is substituted for the dielectric constant at infinite frequency ε_∞. The mole fractions used lie between 0.005 to 0.010.

3. *Results and discussion*

The measured values of $\Delta\varepsilon''/x$ for the investigated phthalazines are given in Table 1. The data are analyzed into two or three Debye terms using the equation[5],

$$\frac{\Delta\varepsilon''}{\Delta\varepsilon_0 - \Delta n_D^2} = \sum_{i=1}^{n} \frac{G_i \omega \tau_i}{1 + \omega^2 \tau_i^2} \tag{2}$$

TABLE 1.

ϱ/GHz	ε''/x				
	A1	A2	A3	A4	A5
0.4	—	—	—	7.263	8.789
0.5	2.040	5.000	4.780	8.046	10.110
0.6	2.320	6.000	5.380	—	10.896
0.7	2.590	—	—	—	—
0.8	2.990	6.460	6.287	8.300	11.700
1.0	3.280	6.650	6.700	7.818	11.472
1.2	3.490	—	6.780	7.334	11.100
1.4	3.700	6.500	6.800	6.917	10.600
1.6	3.800	6.250	—	6.511	10.020
1.7	—	—	—	—	9.868
1.8	3.705	6.000	6.590	6.115	—
2.0	3.740	5.970	6.400	5.857	9.129
3.0	3.400	—	—	—	—
4.0	2.920	4.900	5.660	4.387	6.280
5.0	2.470	4.700	5.210	—	5.515
6.0	2.220	—	4.870	3.630	4.800
7.0	1.900	4.220	4.590	—	4.245
8.0	1.600	3.920	—	2.857	3.753
9.0	1.500	3.840	4.100	—	3.400
10.0	1.370	3.510	—	2.610	3.125
11.0	1.300	—	3.547	—	2.896
14.0	1.094	—	—	—	2.232
15.0	1.030	2.810	3.000	2.020	2.124
$\frac{\Delta\varepsilon - \Delta n_D^2}{x}$	9.50	21.40	22.66	23.75	25.85
$\Delta n_D^2/x$	1.34	1.20	1.12	1.58	2.98

Dielectric data of the different compounds in benzene at 20°C.

TABLE 2.

Compound	$\frac{\mu \times 10^{30}}{\text{cm}}$	$\frac{\tau_1}{\text{ps}}$	$\frac{\tau_2}{\text{ps}}$	$\frac{\tau_3}{\text{ps}}$	G_1	G_2	G_3
A1	8.61	88.42	—	0.61	0.800	—	0.200
A2	12.91	187.24	26.53	0.61	0.542	0.262	0.196
A3	13.28	144.68	26.53	0.61	0.520	0.220	0.260
A4	13.61	244.00	31.83	0.61	0.657	0.160	0.180
A5	14.18	198.90	44.21	0.61	0.821	0.179	0.014

Results of the analysis of the different compounds in benzene at 20°C.

where n is the number of relaxation processes, G_i is the relative weight factor, $\sum_{i=1}^{n} G_i = 1$ and τ_i is the relaxation time. The results obtained are given in Table 2.

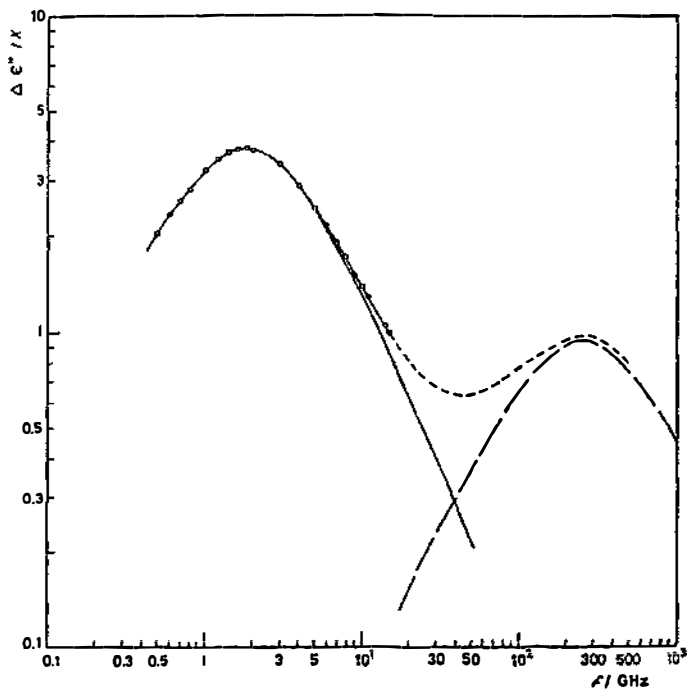


Fig. 1. Dielectric loss $\Delta\varepsilon''/x$ A1 in benzene at 20°C versus frequency.

The τ_1 values are attributed to molecular rotation and are reasonable for molecules of such size. Figs. 1 and 2 show examples of the analysis of the experimental

measurements for the compounds A 1 and A3. It is clear from both figures that the relaxation time τ_1 is accurately defined as the measured points lie on both

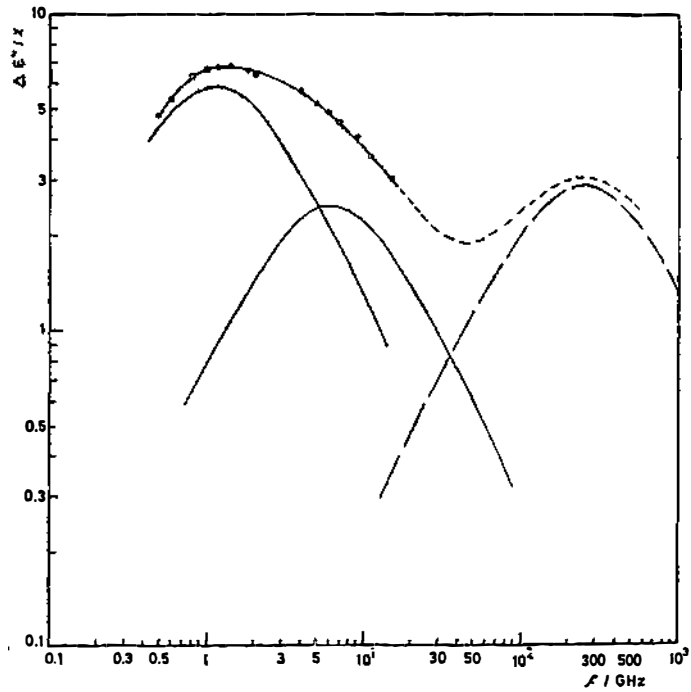


Fig. 2. Dielectric loss $\Delta\varepsilon''/x$ of A3 in benzene at 20 °C versus frequency.

sides of the absorption maximum. The τ_2 values could be due to segmental rotations i. e. to inner mobility in the molecule. This process was not found in case of compound A1 as the molecule is rigid and has no internal mobility. The τ_3 values could be attributed to the Poley resonance absorption[6]. Delker[6] revealed such an absorption for chlorobenzene in cyclohexane in the far infra-red spectrum with a relaxation time τ_p around 0.9 ps which is in agreement with that found here. Anyhow, this third absorption region is obtained by extrapolation. The investigated compounds are used against fungi. The activity of three of these compounds on Aspergillus-niger was determined. A linear relationship as shown in Fig. 3 between the activity of the compound and its internal mobility as represented by the weight factor G_2 was found i. e. the activity is directly proportional to G_2. In a previous work[7], it was interesting to find that the activity is inversely proportional to the effective dipole moment μ given in Table 2. This is not in contradiction to what was found here as G_2 is inversely proportional of μ[8]. This work provides a new method which spares much time in determining the most effective compound from a large number of new compounds.

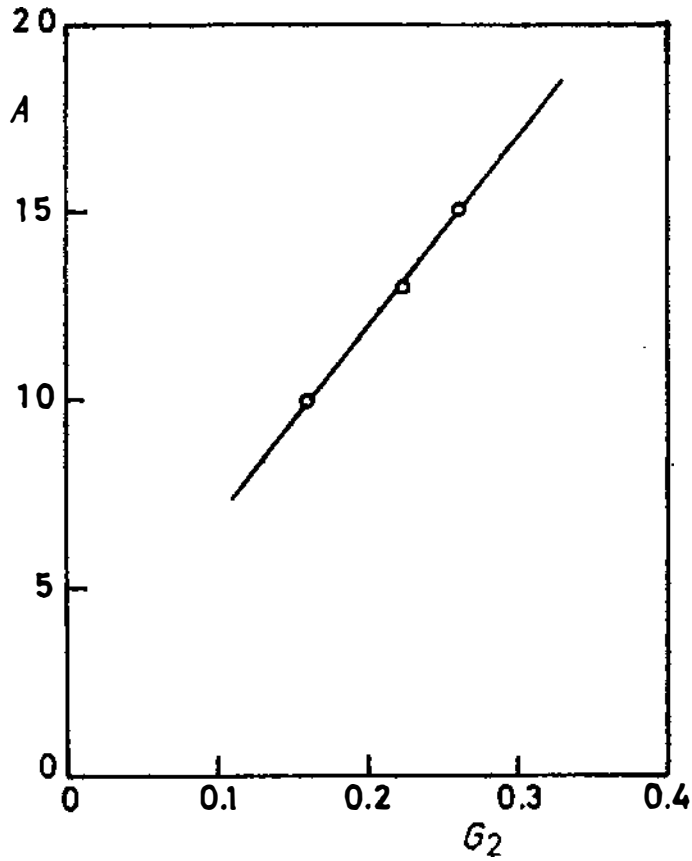


Fig. 3. Variation of the activity of the compound, A (in arbitrary units) with the weight factor G_2

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DIELEKTRIČNA RELAKSACIJA NEKIH NOVO SINTETIZIRANIH AROMATSKIH SPOJEVA IZ MJERENJA MIKROVALNE APSORPCIJE

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Originalni znanstveni rad

Gubitak dielektričnosti ε'' razrijeđenih otopina pet novo sintetiziranih derivata ftalazina u benzenu studiran je u mikrovalnom području između 0,3 i 15 GHz pri 20°C. Analizirani su podaci za tri područja apsorpcije, a objašnjeni su reorijentacijom dipola uslijed molekulske i intramolekulske rotacije. Ispitano je djelovanje tih spojeva na neke plijesni i nađen je linearni odnos te aktivnosti i intramolekulske orijentacije tih spojeva.