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Electrical and X-Ray Diffraction Studies of Some New Organic Compounds

Dr. A.S. El-Hiti, Dr. N.Molekhiah and Dr. M.A.Issa

Physics Dept., King Saud University, Riyadh, Saudi Arabia.

The electrical behaviour of some compounds of aromatic sulphonamide derivatives has been investigated. The temperature dependence of the dielectric constant and loss tangent were recorded. An x-ray diffraction analysis was also carried out and a trial has been made to correlate between the electrical measurements and x-ray analysis.

In the last few years organic compounds began to attract the attention of many eminent physicists. This may be due to their interesting behaviour as catalysts or due to the ability to use some of them as lasting elements. Extensive research work has been done on the electrical properties of these compounds in an effort to relate electrical behaviour to chemical structure. Okamoto *et al.*[1] have measured the electrical properties of simple polycyclic aromatic hydrocarbons (*e.g.* anthracene, naphthalene). These measurements were made in accordance with the techniques developed by Brown and Aftergot[2].

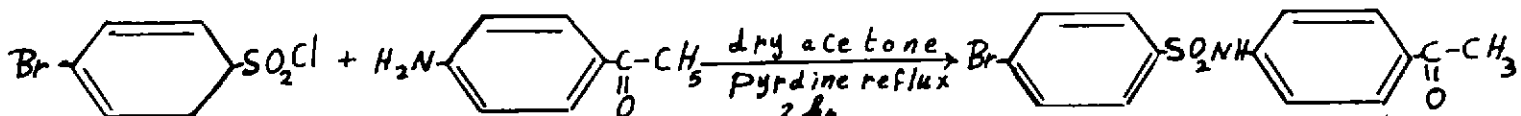
The present work has been carried out to study the electrical properties of these four aromatic sulphonamide compounds. X-ray studies were used for identification and to throw more light on the relation between their structures and the chemical activity characterizing these compounds. X-ray analysis was also carried out to follow any phase transformation which might be developed due to the heat treatment.

Specimen Preparation

The four organic compounds under investigation were prepared by Morad[*] according to the following reactions:

* Chem. Dept. Ain Shams University, Cairo

(A)



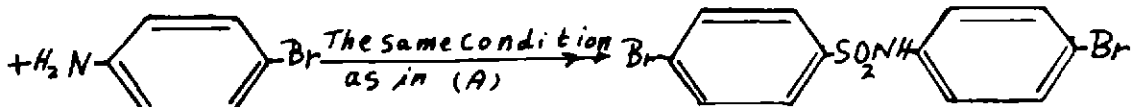
P-Bromobenzene sulphonyl chloride

P-amino acetophenone

4-Bromobenzene sulphon-4-acetylanilide

(B)

P-Bromobenzene Sulphonyl Chloride

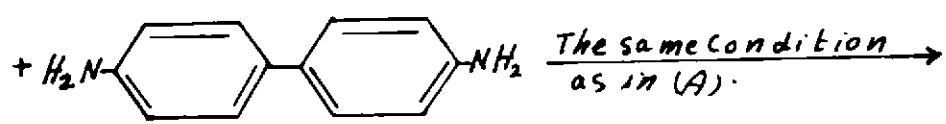


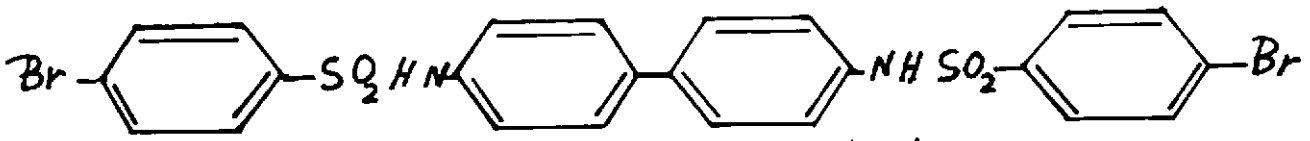
P-Bromoaniline

4-Bromobenzene sulphon-4-bromoanilide

(C)

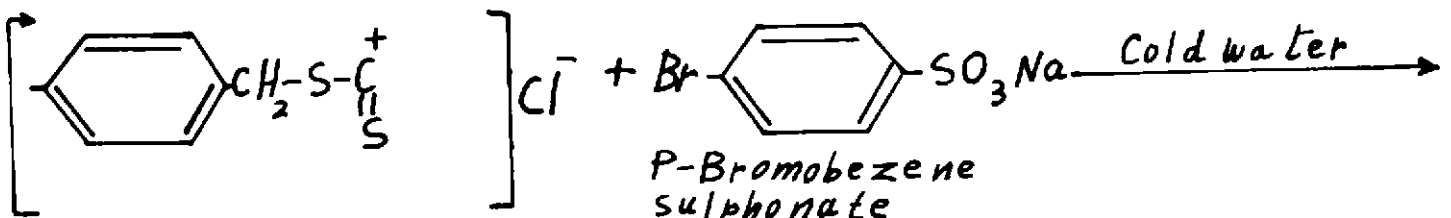
P-Bromobenzene sulphonyl chloride (2 moles)





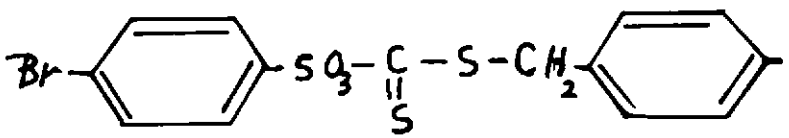
Bis(p-Bromobenzene sulphanilyl) biphnyl

(D)



S-Benzyl thiouronium chloride

P-Bromobezene sulphonate



S-Benzyl thiouronium-p-bromobenzene sulphonate

These compounds were marked by letters A,B,C, and D respectively. The melting point of each compund was measured and was found to be: 195, More than 250,225 and 186°C respectively.

Specimens Preparation for Electrical Studies

The polycrystalline organic compounds were pressed into tablets with diameter 1.2cm and thickness 2-3mm at pressure 3 tons/cm^2. The samples were then exposed to a flow of dry air to remove any attached particles or moisture. Two silver electrodes were then made on the major faces using silver paints.

Experimental

1. Dielectric Properties

The dielectric constant and the loss tangent of the four organic compounds were determined by measuring the capacity of the samples on a bridge type B641 (Wayne Kerr). Measurements were done in the range 20-170°C at normal frequency of the bridge (1.5 KH_z). Beyond this temperature the electrodes started to dissociate. The results are shown graphically in Fig. (1&2). The effect of frequencies on the dielectric properties were studied and illustrated in Fig.(3). Measurements of electrical conductivity were carried out by a two probe method of placing-known voltage across the specimen and measuring the current with a nanoameter type Philips PM 2435. The results are shown in Fig.(4).

2. X-Ray Studies

A beam of x-rays is diffracted by a crystal when certain geometrical conditions are satisfied. The conditions may be stated either by Laue's equations or by Bragg's law. With the help of the latter the position of the diffraction beams forming the diffraction pattern can be analysed.

The materials under test were finely ground. The samples were in the powder form with grain size suitable for study by the x-ray diffraction methods. For the purpose of identification of the compounds by x-ray diffraction methods, a small amount of material 0.2-0.4mm in linear dimensions was packed as tightly as possible in a thin glass capillary. For the diffractometer techniques, the specimens holder of the diffractemeter. The diffraction patterns were recorded using Philips powder camera (114.6mm diameter), Philips diffractometer and generator with filtered copper radiations. The materials A,B,C and D were heated to 180,200,200 and 175°C respectively, for half an hour and cooled to room temperature. The diffration patterns were recorded again under the same conditions. The results were compared with a standard data from the A.S.T.M. cards. The intensities were measured qualitatively by designating each line as strong (S), medium (M), weak (W), very weak (V.W), faint (F) and very faint (V.F.). Table (1) shows the interplaner spacings of the four compounds.

Discussion and Conclusion

Dielectric properties and x-ray diffraction methods were used in this work to study some new compounds of aromatic sulphonamide derivatives.

The dielectric constant (ε) and loss tangent ($\tan\alpha$) of the four compounds were measured as function of temperature from 20°C to 170°C at a frequency of 1.5 KH_z. The results were illustrated in Fig. (1&2). It is clear that the dielectric constant of the compounds A,B and C is nearly independent of temperature in comparison with the compound D. The dielectric constant of A,B and C increased from 10 at room temperature to 25 at 170°C. On comparing these values with the compound D, it varies from 18 to 210 through this range of temperatures.

The effect of high frequencies on the dielectric constant of the compound D was studied and was illustrated in Fig. (3). On increasing the frequency from 1.5 KH_z to 10 and then to 100 KH_z the dielectric constant decreased and became nearly independent of temperature.

The polarization existed in such compounds plays a great role in the dielectric behaviour. It is known that most of organic compounds have large displacements of charges in their structures[4]. The dislocation of the charges in the cation causes an effective change in the dipole moment of these compounds and hence the polorization. The increase in (ε) with temperature may be due to dipolar rotation or imperfections affecting space charge polorization.

The change of the loss tangent with temperatures was illustraled in Fig.(2). It increased with temperature showing that these materials are unlikely to be used as dielectric medium in capacitors. The loss tangent of the compound D was strongly affected by temperature in comparison with the others. Its value increased from 0.005 at 20°C to 0.37 at 120°C.

The electrical conductivity of these materials has been studied as a function of temperatures. The conductivity of the compounds A,B and C was found to be slightly increased with temperature while the conductivity of the compound D is highly affected as shown in Fig. (4). The increase in conductivity, or the decrease in the resistivity, with temperature characterize the materials, in general, as a semiconductor which is the case in the compounds A,B & C. The high increase in the conductivity of the compound D with temperature may suggests that this material is ionic conductor. In that case, the intermolecular forces are very week and are highly disturbed by increasing temperature.

X-ray studies were carried out to identify these organic compounds and to follow the phase transformation (if any) at elevated temperatures. These results showed that the lattic spacings of the two components forming each reaction were not observed in the patterns of the last compound. It means that these reactions were completely occurred. The interplaner spacings of the new formed compounds were measured and tabulated in Table 1. The patterns were compared with the A.S.T.M. cards. It was found that no information on x-ray diffraction patterns of these four compounds was recorded uptill now. It means that there is no x-ray information on their interplaner spacings and the geometry of the crystals forming these compounds.

The diffraction patterns of the specimens preheated to 180,200,200 and 175°C for compounds A,B,C and D respectively, showed that no phase transformation

formed at these particular temperatures. Fig.(5) showed the diffraction patterns of the compound D before and after heating to 170°. This compound was chosen because it showed anomalous electrical properties in comparison with the other compounds.

To relate the electrical behaviour and the geometry of these crystals the complete picture of the structure determination must be given. The structure determination of the crystal needs hard work and x-ray special studies belonging to single crystal analysis for indexing, rotation, oscillation and Weissenberg patterns.

Aknewledgment

This work has been done at physics Dept., College of Science University of Riyadh, Saudi Arabia. The authors would like to thank Dr.Morad for preparing the investigated compounds.

References

1. **Okamoto, Y., Brophy, J.J., and Buttrym J.W.** *Organic Semiconductors*, p. 100, 1962.

2. **Brown, G.P., and Afterget, S.,** *Proc of Princeton University Conference on Semiconduction in Molecular Solids*, 1960.

3. **Smyth, C.P.,** *Dielectric Behaviour and Structure*, New York, McGraw Hill, 1955.

Table (1): The interplaner spacings of the four compounds.

Sample A		Sample B		Sample C		Sample D	
d A°	I/I_0	d A°	I/I_0	d A°	I/I_0	d A°	I/I_0
10.64	M	15.76	V.W	11.41	M	18.42	M
7.10	W	7.25	W	8.54	M	10.52	V.F
6.45	V.F	5.67	W	6.10	W	9.50	W
5.86	V.F	5.15	W	5.57	M	8.50	F
5.52	M	5.09	W	5.21	V.W	7.13	F
5.27	W	4.79	W	5.02	W	6.32	M
4.91	F	4.28	F	4.82	W	5.75	W
4.76	S	4.11	F	4.43	W	5.27	W
4.59	M	3.86	V.W	4.24	W	4.92	W
4.36	F	3.66	W	4.18	W	4.75	V.S
4.27	W	3.26	W	3.95	V.W	4.31	M
4.19	V.F	3.14	F	3.80	V.S	4.19	S
4.08	S	2.91	F	3.64	W	4.00	W
3.98	M	2.84	V.S	3.49	W	3.93	W
3.90	V.F	2.43	V.F	3.37	W	3.83	S
3.57	M	2.35	V.F	3.26	W	3.70	W
3.53	V.S	1.99	M	3.09	W	3.64	W
3.46	W	1.70	V.F	2.85	W	2.56	M
3.38	F	1.63	W	2.78	V.W	3.35	W
3.32	V.W	1.41	W	2.64	F	3.25	F
3.21	V.F	1.26	W	2.63	F	3.18	W
3.18	W	1.15	W	2.61	F	3.16	F
3.11	W			2.36	V.F	3.07	M
3.08	M			2.24	V.F	3.03	M
3.00	V.W					2.94	F
2.93	V.W					2.86	V.F
2.85	V.W					2.79	V.F
2.77	V.W					2.74	W
2.75	F					2.69	W
2.64	W					2.59	V.F
2.62	W					2.51	F
2.56	W					2.46	V.F
2.50	V.W					2.40	W
2.42	F					2.38	M
2.37	W					2.33	M
2.34	F					2.28	V.F
2.28	V.F					2.13	M
2.20	W					2.10	V.F

Sample A		Sample B		Sample C		Sample D	
2.09	W					1.99	F
2.07	W					1.93	W
2.03	W					1.88	W
1.99	V.F					1.82	W
1.95	V.F					1.78	V.F
1.91	V.F					1.74	F
1.88	V.F					1.72	V.F
1.80	V.F					1.65	V.F
1.74	V.F					1.63	V.F
						1.61	V.F
						1.60	W
						1.58	W

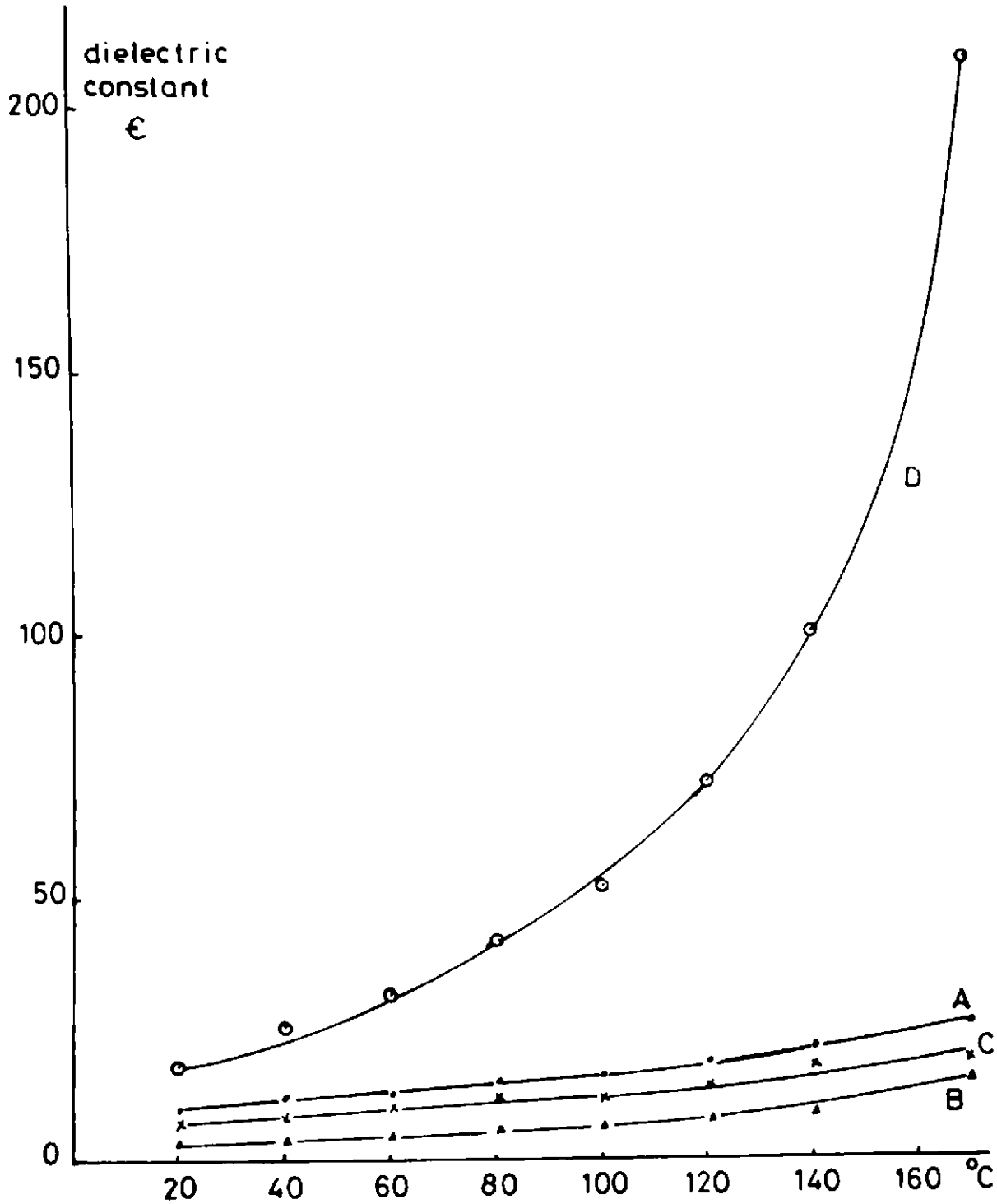


Fig. 1 The temperature dependance of the dielectric constant for the compounds A,B,C & D.

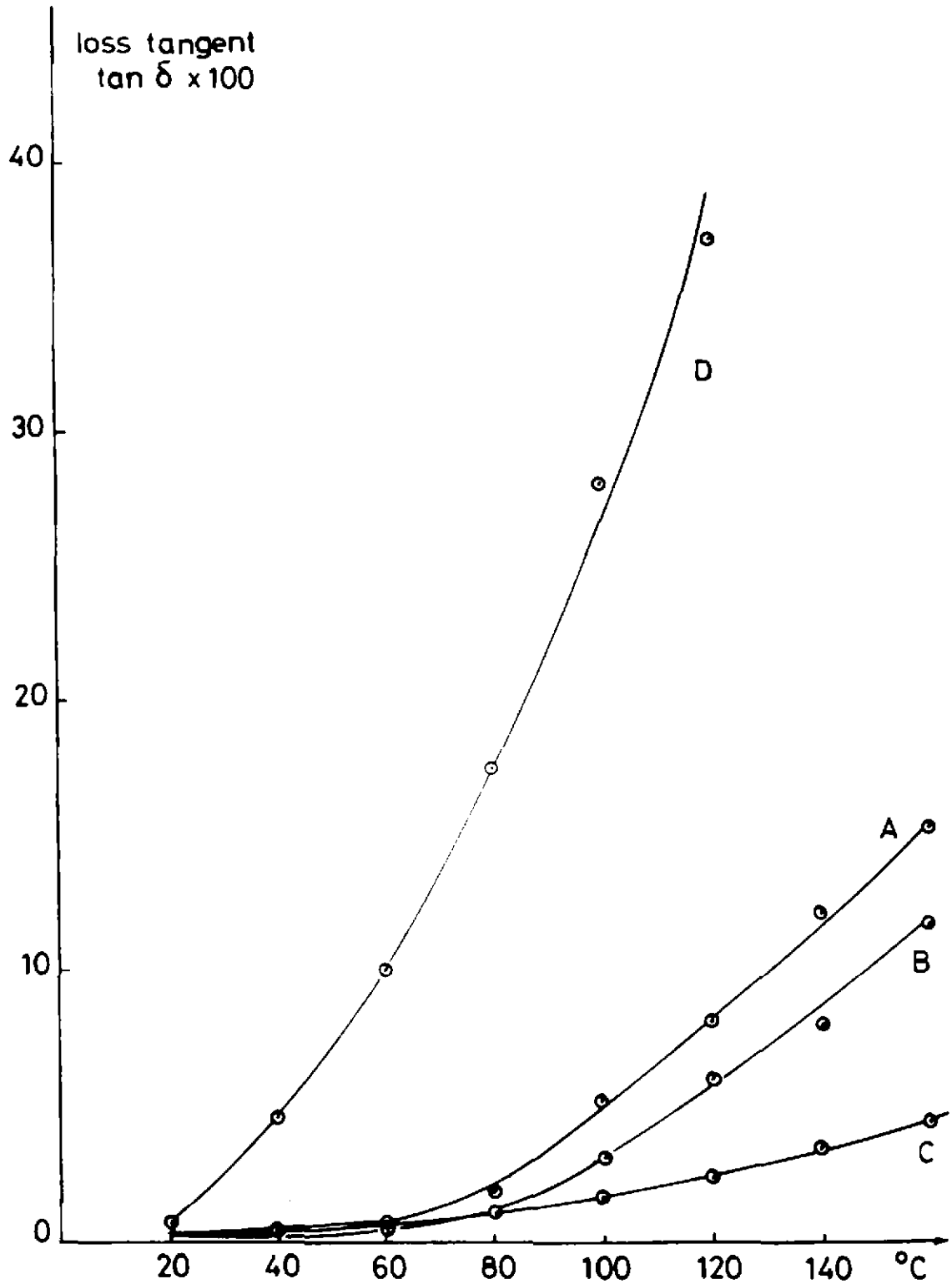


Fig. 2 The temperature dependance of the los'tangent for the compounds A,B,C & D.

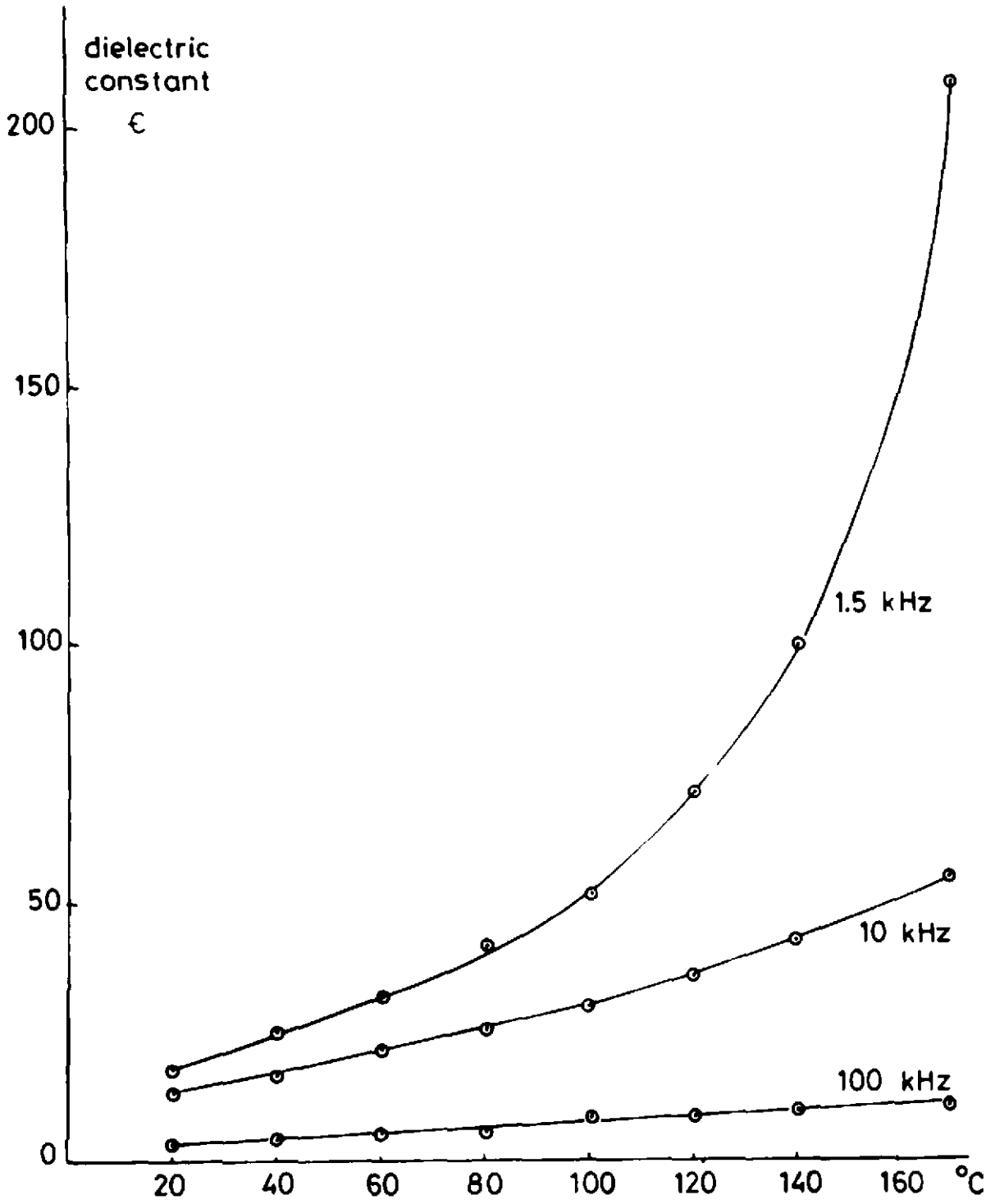


Fig. 3 Variation of dielectric constant with temperature for the compound D at different frequencies.

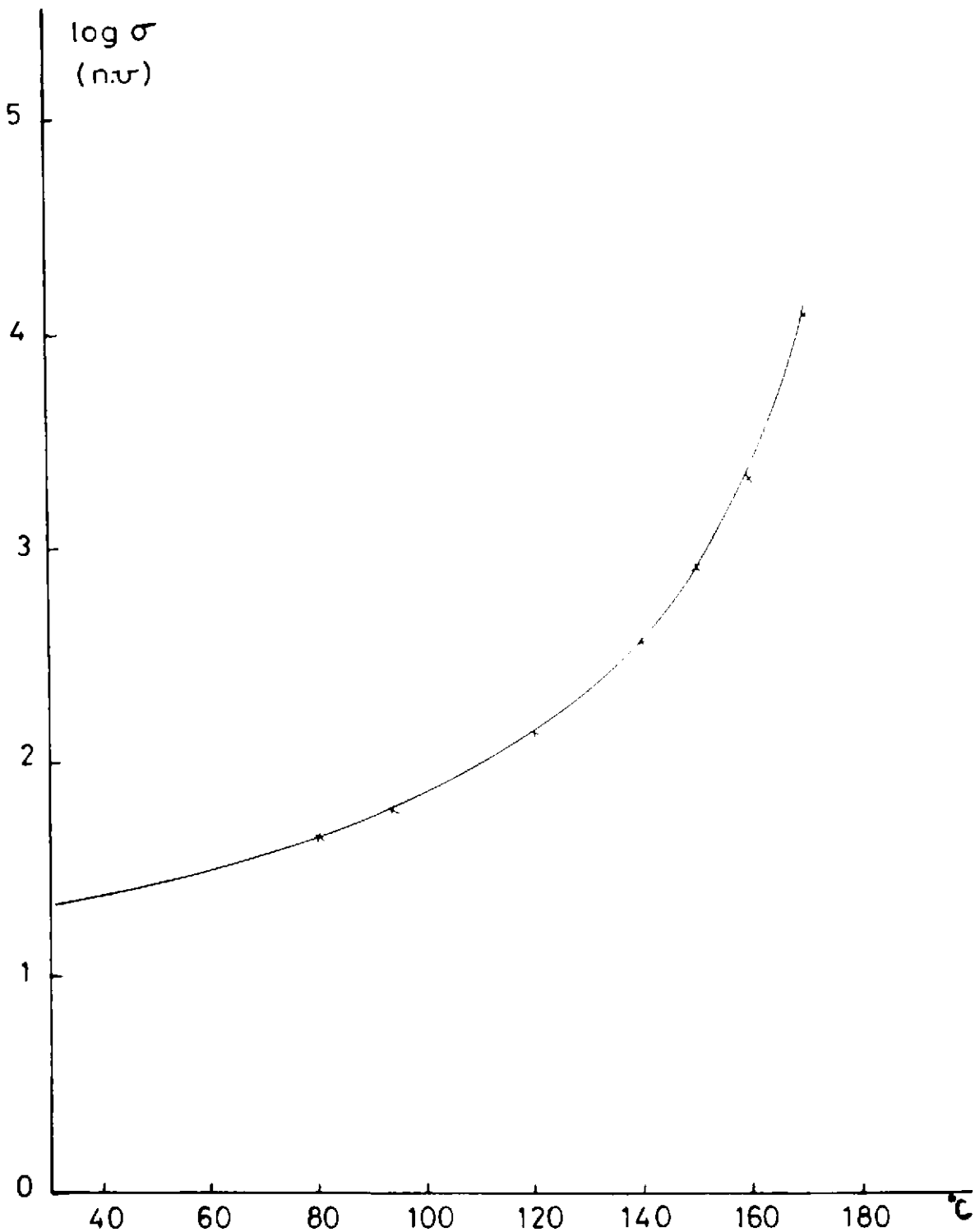


Fig. 4 The electrical conductivity of the sample (D) as a function of temperature.

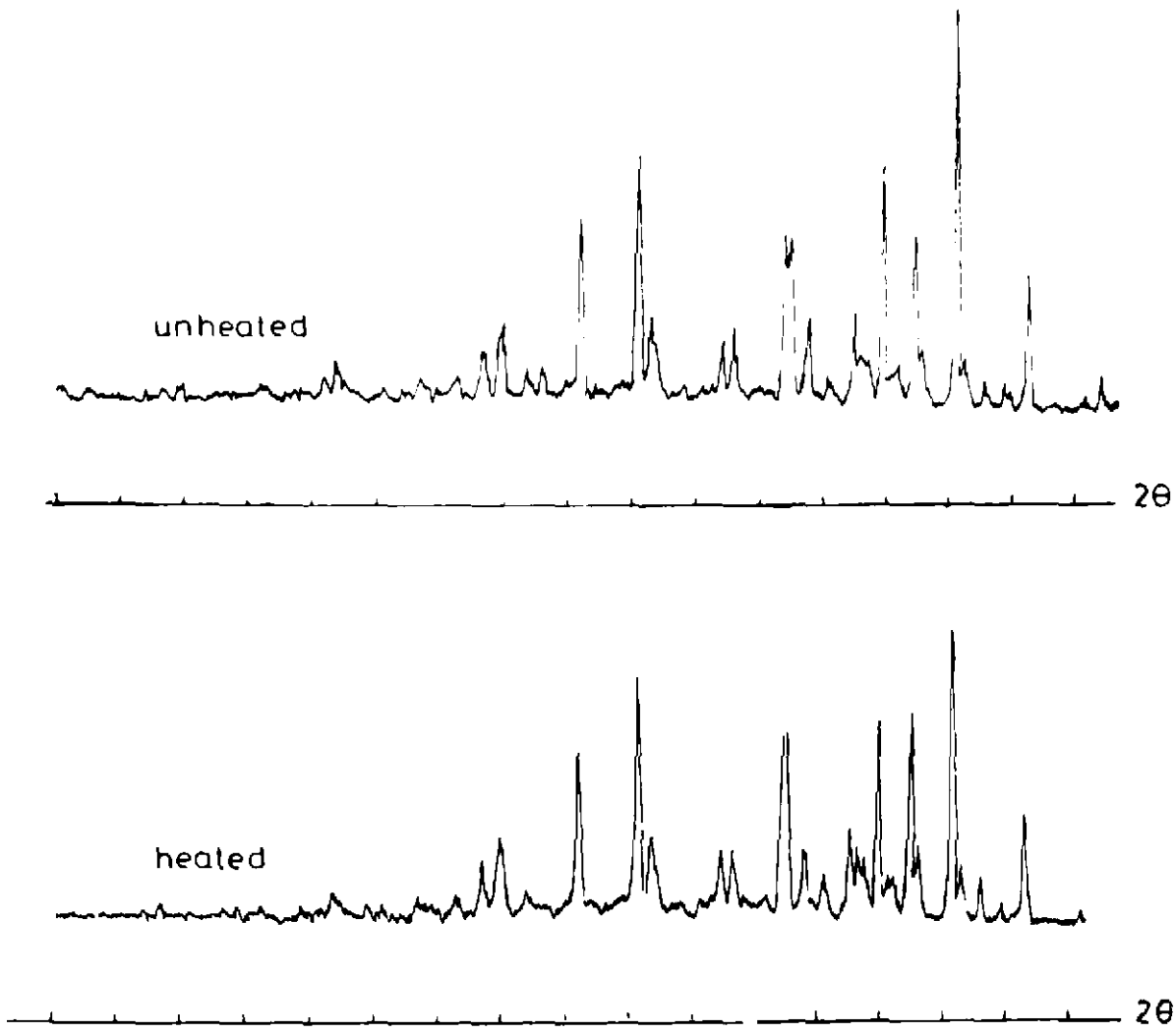


Fig. 5 X-Ray diffraction lines of the sample D.

دراسة الخواص الكهربائية وحيود الأشعة السينية لبعض المركبات العضوية الجديدة

الدكتور عبدالعزيز سالم الهيتي، الدكتور نبيل محمود ملوخية،
الدكتور حمد علي عيسى

قسم الفيزياء ، كلية العلوم ، جامعة الملك سعود.

تناولت هذه الدراسة تعيين المسافات البينية لبعض مشتقات مركبات السلفواميد العضوية الجديدة كما درست الخواص الكهربائية لهذه المركبات ثم تم الربط بين الخواص الكهربائية والتركيب البلوري لها.