

minutes. The cold melt was leached with water (100 c.c.) and the solution was filtered. The filtrate was chilled to about 10° C. and acidified with hydrochloric acid till it was acid to congo red. The aminosalicyclic acid which had separated was extracted with ether and ether extract dried with anhydrous sodium sulphate. On removal of ether the acid separated out as a light cream coloured powder; yield 2.8 g. The acid was crystallised from alcohol, m.p. 145-46° (decomp.). Hydrochloride m.p., 220-21°. Found: N, 9.0, 9.2; C₇H₇O₃N requires 9.15%.

When fusion was conducted using solid paraffin (20 g.) as a diluent, almost the same yield of *p*-aminosalicylic acid was obtained. The acid gives a purple colouration with alcoholic ferric chloride and liberates carbon dioxide from sodium bicarbonate solution. The acid is sparingly soluble in water and moderately soluble in cold alcohol and ether. On heating, the acid gets decarboxylated to *m*-aminophenol. These findings are interesting when viewed in the light of the observation of J. A. Connor¹⁰ that aqueous solution of *p*-aminosalicylic acid or its hydrochloride is decarboxylated to *m*-aminophenol at temperatures above 80° C.

Attempts to hydroxylate the nitro sulphobenzoic acid by fusion with potassium hydroxide yielded only a charred product from which nothing definite could be isolated. Such decompositions of nitro compounds during alkali fusion are known.¹¹

Full experimental details will be published elsewhere.

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1. Lehmann, *Lancet*, 1946, 250, 15. 2. Youmans, *Quart. Bull. North-Western Univ. Med. School*, 1946, 20, 420. C.A., 41, 1011. 3. Martin, D. D., *et al.*, *Nature*, 1948, 161, 435. 4. Siedel and Bittner, *Monatsh*, 1902, 23, 423. Kondo, H. and Nakajima, T., *J. Pharm. Soc., Japan*, 1922, 485, 355. 5. Ullmann and Wagner, *Ann.*, 1907, 355, 360. "Beilsteins Handbook," 14, 592. *Ann.*, 1912, 390, 4. 6. John, T. Sheehan, *J. Amer. Chem. Soc.*, 1948, 70, 1665. Erlenmeyer, *et al.*, *Helv. Chimica Acta*, 1948, 31, 988. Martin, D. D., *et al.*, *Nature*, 1948, 161, 435. 7. Hart, *Am. Chem. J.*, 1, 350. 8. Kastle, *Ibid.*, 1899, 11, 179. 9. Hedrick, *Ibid.*, 9, 411. 10. Connor, J. A., *Lancet*, 1948, 254, 191. 11. "The Synthesis of Benzene Derivatives," by S. C. Bate, 1926, p. 154.

DIELECTRIC CONSTANT OF IONIC SOLIDS

THE application of Debye Clausius Mosotti equation to the high dielectric constant of solids has been shown to be theoretically unsound and practically hopeless.

Even for alkali halides no theoretical calculation of the dielectric constant is possible, because of the difficulty in estimating the internal field in a crystal (*cf.* Mott and Gurney, 1940). One of us (S.K.K.J., 1944) has put forth a theory based upon the parallel and anti-parallel orientation ($2J+1=2$) in liquids and solids in a needle-shaped cavity, which yields an extraordinarily simple relationship (I) between the dielectric constant and dipole moment:

$$(\epsilon - n_{\infty}^2) \frac{M}{d} = 4\pi N u^2 / 3KT \left(\frac{J+1}{J} \right) \dots (I)$$

In the case of associated liquids like water, alcohols and ionic solids (rochelle salt, BaTiO₃) showing transition the characteristic temperature θ must be taken into account.

We have applied the above equation to the dielectric constants of alkali halides. The results are shown in Table I. The ionic character (*i*) as calculated by the ratio of the observed dipole to the full moment is found to be about 5% for all the alkali halides.

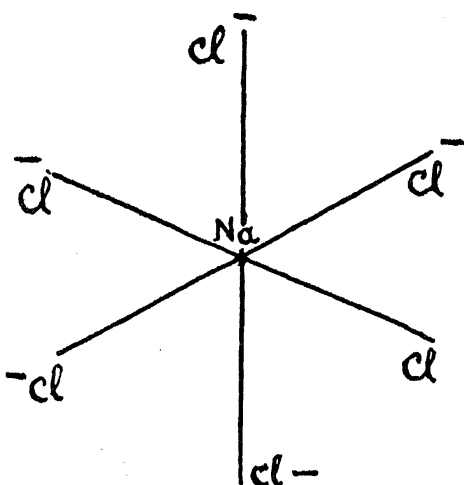
Dielectric Constant and Dipole Moments of Alkali Halides

	ϵ	n_{∞}^2	d	μ	i	$6A \times i$
NaCl ..	5.6 (1) 5.83 (4)	2.38	2.16	0.68 0.70	0.050 0.052	.52 .55
NaBr ..	6.1 (2) 6.39 (3)	3.08	3.20	0.72 0.75	0.049 0.052	.51 .55
KCl ..	4.5 (1) 4.8 (4)	2.22	1.97	0.67 0.71	0.045 0.047	.47 .49
KBr ..	4.6 (2) 4.7 (5)	2.43	2.75	0.70 0.72	0.045 0.046	.47 .48
RbCl ..	4.68 (1) 4.78 (4)	2.23	2.76	0.76 0.77	0.048 0.049	.50 .51
RbI ..	4.51 (4) 5.0 (7)	2.72	3.55	0.75 0.88	0.043 0.050	.45 .52

1. P. Schupp (1932); 2. Staulmann (1932); 3. S. Kyropoulos; 4. K. Højendahl (1933); 5. Heydweiller (1921); 6. Starke (1897); 7. Mott and Gurney (1940).

These results can be quantitatively explained on the basis of the concept of covalent-ionic resonance postulated by

Pauling without reference to his electro-negativity theory. If we consider a six bonded unit NaCl_6 or ClNa_6



and that only one bond of the six, is covalent and the remaining *fully* ionic, the dipole moment due to four mutually perpendicular ionic bonds will cancel as they oppose in pairs

the remaining $\overset{-}{\text{Cl}}\overset{+}{\text{Na}}:\overset{-}{\text{Cl}}$ will give 0.5 ionic character for a total of six NaCl bonds. If we assume that the influence of surrounding bonds is given by Madelung constant A just as in the case of bond energy, the effective ionic character for six NaCl bonds will be $6 \times A$ times the apparent ionic character of each bond. The results in the last column for a range of the alkali halides are in agreement with the theoretical value 0.5.

The above concept that only one bond out of six is covalent in character gives $5/6$ or 83% as the value of the ionic character of alkali halides which is supported by the data on crystal energy, magneto optic anomaly, &c., as will be shown in a separate note.

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1. Mott and Gurney, *Electronic Processes in Ionic Crystals*, p. 22, 1940. 2. Jatkar, *Nature*, 1944, 153, 222.

ON THE PREPARATION OF PALUDRINE (PROGUANIL)

FOLLOWING the discovery of Paludrine,¹ sufficient interest has been developed in the field of substituted biguanides as potential antimalarials. For the chemical synthesis of substituted biguanide derivatives, a number of methods¹⁻⁶ are available,

the simplest being the condensation of a substituted cyanoguanidine with an amine. For the synthesis of N^1 -aryl- N^5 -alkyl-biguanides the reaction between aryl-cyanoguanidine and alkylamine has been successfully conducted in the presence of copper sulphate or by fusion (using salt of the amine) but the desired products are not formed when the reactants are refluxed with alcohol.

During the course of investigations of N^1 -aryl- N^5 -heterocyclic biguanides,⁴ we were unable to condense certain substituted amino-heterocyclics (using hydrochloride salts) with arylcyanoguanidines in boiling alcohol. Considering that this reaction temperature may not be sufficient for reaction, iso-amyl alcohol was used instead in order to give reaction temperature of about 140°C . Although, no success was encountered in the above cases, the same procedure has been successfully employed for the preparation of paludrine as follows:

p-Chlorophenylcyanoguanidine (5 g.) and isopropylamine hydrochloride (3 g.) were refluxed together in isoamyl alcohol (15 c.c.) in an oil-bath maintained at 150°C . for 14 hours. The reaction mixture was extracted with boiling water and the aqueous portion was concentrated and chilled. Paludrine hydrochloride was collected by filtration and dried. Yield 1.5 g.; m.p. 244° .

Curd, *et al.*² have also recently prepared N^1 -*p*-fluorophenyl- N^5 -isopropyl-biguanide hydrochloride by a similar procedure, using nitrobenzene as solvent. In my experiment, replacement of iso-amyl-alcohol by nitrobenzene gave paludrine hydrochloride (3 g.), m.p. 244° .

Attempts are being made to improve the yield still further by varying the solvent and the experimental conditions.

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1. Curd and Rose, *J. Chem. Soc.*, 1946, 729.
2. Curd, *et al.*, *Ibid.*, 1948, 1630. 3. Bami and Guha, *J. Indian Inst. Sci.*, 1949, 31A, 1. 4. —, *Ibid.*, 9. 5. Fernandes and Ganapathi, *Proc. Indian Acad. Sci.*, 1948, 28A, 563. 6. Crowther, *et al.*, *J. Chem. Soc.*, 1948, 1636.