NOTES.

The Electric Polarisation of Flexible Molecules. By N. R. Davidson and L. E. Sutton.

Coop and Sutton (J., 1938, 1269) recently discussed the nature of the large polarisations found for the vapours of a number of flexible molecules. It appeared that one or both of two processes are responsible, these being (1) a process of distortion from the equilibrium position by the field, *i.e.*, atom polarisation; (2) a process of orientation, in the applied field, of bent molecules. It was argued that, if the natural period of bending were less than the relaxation time for orientation (assumed to be about 5×10^{-12} sec.), then only atom polarisation would occur; but if it were larger, both would occur. It is the object of this note to show that these processes do not make independent contributions to the total polarisation.

Using the classical treatment, and neglecting momentum co-ordinates, we have the following expression for the mean polarisation of a flexible molecule :

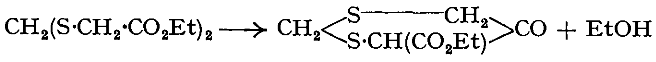
$$P = \frac{4\pi\boldsymbol{N}}{3} \frac{\int \mu(\psi) e^{-V(\psi)/\boldsymbol{k}T + \mu(\psi)E\cos\theta/\boldsymbol{k}T} \cos\theta \,.\, d\psi \,.\, \sin\theta \,.\, d\theta \,.\, d\phi}{\int e^{\ V(\psi)/\boldsymbol{k}T + \mu(\psi)E\cos\theta/\boldsymbol{k}T}\, d\psi \,.\, \sin\theta \,.\, d\theta \,.\, d\phi}$$

where $\mu(\psi)$ is the moment of the molecule for an internal configuration ψ, $V(\psi)$ is the potential energy expressed as a function of ψ, θ is the inclination of the instantaneous moment of the molecule to the axis of the applied field E, and ϕ is the remaining angular co-ordinate for the three-dimensional problem. The exponential index includes the ratios both of the internal potential energy and of the potential of the instantaneous dipole in the field to $\boldsymbol{k}T$. It therefore gives the effect both of temperature and of the field on the average internal and external configurations of the molecule; and it brings in the averaging processes employed in the " thermal bending " treatment (equation 1; Finn, Hampson, and Sutton, J., 1938, 1261), in the atom polarisation treatment (*e.g.*, Coop and Sutton, J., 1938, 1281), and in deriving the polarisation for a permanent dipole, since $\mu(\psi)$ could include a constant term. Thus, it gives the complete polarisation, except for electron polarisation which would require further internal co-ordinates and potential functions, so long as the frequency of the applied field is sufficiently small for all modes of polarisation to contribute. In the particular case considered by Coop and Sutton, where the molecule contains two equal and opposed dipoles, each μ_1, and has a potential function $V(\psi) = V_0\psi^2/2$, the value of the expression is $4\pi\boldsymbol{N}\mu_1^2/9V_0$. This is the magnitude which was assigned *either* to the so-called " thermal bending " polarisation *or* to the atom polarisation, but it is now clear that it is the total effect, so the dynamic processes of orientation and of distortion which underlie these do not contribute equally and independently to the total polarisation. In fact, the above statistical method does not distinguish between them.

From the dynamical point of view it seems that, if the force constant and, hence, the frequency of vibration are large enough, the main effect of the field is to shift the mean position about which vibration occurs; the resulting polarisation may therefore appropriately be called atom polarisation. When, however, the force constant is small, it appears that in general the polarisation cannot be adequately described either as atom polarisation or as thermal bending polarisation in the restricted sense of these terms as used above. In most known cases the force constants and frequencies of vibration are so large that it is a good approximation to the truth to use the term atom polarisation. The only probable exceptions are some molecules of the ethylene dichloride type, and these warrant a separate discussion.—The Dyson Perrins Laboratory, Oxford. [*Received, December 9th,* 1938.]

The Self-condensation of Ethyl Methylenebisthioacetate. A New Method for the Preparation of Derivatives of 1 : 3-*Dithian.* By Frederick Challenger and Samuel A. Miller.

For the purposes of another investigation the condensation of the ethyl esters of methylenebisthioacetic acid (8 g.) (Holmberg and Mattisson, *Annalen*, 1907, **353**, 125; Holmberg, *Ing. Vetensk. Akad. Handl.*, 1930, **103**, 5) and mesoxalic acid (6 g.) by means of sodium (3 g.) in alcohol (60 c.c.) was attempted. The mixture became warm and somewhat brown and soon deposited a solid. After 5 days water was added, and the alkaline solution extracted with ether (removing only a little resin) and acidified. Ether extraction yielded an oil which partly solidified below 0°. Recrystallisation of the solid portion from aqueous alcohol gave a white product (A), m. p. 62°. This compound was also obtained (B) when the reaction was carried out as above but in absence of the ethyl mesoxalate [Found for (A) : C, 41·2; H, 4·9. Found for (B) : C, 41·1; H, 5·0; S, 31·2. $\mathrm{C_7H_{10}O_3S_2}$ requires C, 40·8; H, 4·9; S, 31·1%]. The compound is therefore formed by the self-condensation of ethyl methylenebisthioacetate in a reaction of the Dieckmann type, giving *ethyl* 1 : 3-*dithian*-5-*one*-4-*carboxylate* :



$$\mathrm{CH_2(S{\cdot}CH_2{\cdot}CO_2Et)_2 \longrightarrow CH_2{<}\begin{matrix}S\text{———}CH_2\\ S{\cdot}CH(CO_2Et)\end{matrix}{>}CO + EtOH}$$

It formed a bright yellow 2 : 4-*dinitrophenylhydrazone*, m. p. 147° after four recrystallisations from alcohol (Found : C, 40·6; H, 3·7; N, 14·5; S, 16·4. $\mathrm{C_{13}H_{14}O_6N_4S_2}$ requires C, 40·4; H, 3·6; N, 14·5; S, 16·6%), and a semicarbazone. Hydrolysis of the ester with 2N-sodium hydroxide caused ring fission and regenerated methylenebisthioacetic acid, m. p. (after four recrystallisations from toluene) and mixed m. p. 127° (Found : S, 32·2. Calc. : S, 32·6%). It gave an insoluble yellow ferric *salt* (Found : Fe, 16·7. $\mathrm{C_{15}H_{18}O_{12}S_6Fe_2}$ requires Fe, 16·2%).

Addition of sodium ethoxide to an alcoholic solution of the ester gave a solid sodium derivative, from which the ester was recovered unchanged on addition of water. Ferric chloride gave a violet colour. Bromine water was added until this was just discharged. The colour reappeared after a few moments.

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Condensation of Benzylidene Chloride with o-*Xylene.* By Edward de Barry Barnett.

Ellison and Hey (J., 1938, 1847) have shown that the phenyl group is not present in the anthracene derivatives obtained when benzaldehyde is condensed with the xylenes in the presence of aluminium chloride. This is not the case when benzylidene chloride is condensed with *o*-xylene, as, in addition to much tar, 9 : 10-*diphenyl*-2 : 3 : 6 : 7-*tetramethylanthracene* is formed.

Finely powdered aluminium chloride (30 g.) was added with water-cooling during 3 hours to 25 c.c. of *o*-xylene and 50 c.c. of benzylidene chloride in 100 c.c. of tetrachloroethane. After the product had been kept overnight, volatile matter was removed with steam, and the resulting tar repeatedly extracted in the cold with alcohol, benzene, and finally with acetone. The residue, after being recrystallised from benzene and from anisole, was pale yellow and had m. p. 312° (Found : C, 93·2; H, 7·1. $\mathrm{C_{30}H_{26}}$ requires C, 93·2; H, 6·8%). The yield was 1·5 g. —Sir John Cass Technical Institute, London. E.C.3. [*Received, December 29th,* 1938.]

Mononitration of α- *and* β-*Naphthylamines in the Presence of Urea.* By Herbert H. Hodgson and William Davey.

Meldola and Streatfeild (J., 1893, **63**, 1054) obtained only 6—8% of 8-nitro-1-naphthylamine by nitrating α-naphthylamine in sulphuric acid solution. Morgan and Jones (*J. Soc. Chem. Ind.*, 1923, **42**, 341 T), by an improved process, increased the yield to 16—18%. α- and β-Naphthylamines have now each (14 g.) been nitrated in concentrated sulphuric acid in the presence of urea, with the following results :

Nitric acid, % of the amount required for mononitration.	Nitro-1-naphthylamines.				Nitro-2-naphthylamines.			
	8-Nitro-.		5-Nitro-.		8-Nitro-.		5-Nitro-.	
	G.	%.	G.	%.	G.	%.	G.	%.
100	5	27·1	8	43·3	1	5·4	16	86·7
80	2	10·8	7	37·9	1	5·4	16	86·7
75	1	5·4	6	32·5	Trace		8	43·3
200	6	32·5	7	37·9	Trace		13	70·5

In the products of nitration of phthalo-α- and -β-naphthylimides (Hodgson and Crook, J. 1936, 1844) the ratio of 8-nitro- to 5-nitro-1-naphthylamine is 15 : 7, and of 8-nitro- to 5-nitro-2-naphthylamine is *ca.* 11 : 10.

Mononitration of α-*Naphthylamine.*—(a) *With the theoretical amount of nitric acid.* Urea (7 g.) and α-naphthylamine (14 g.) were dissolved in this order in concentrated sulphuric acid (100 c.c.) and the externally ice-cooled solution was treated gradually with finely powdered potassium nitrate (11 g.); the mixture was then stirred for 1½ hours and poured on ice (200 g.). The precipitated base, which was free from tar, was collected and twice extracted with 10% hydrochloric acid (1 l., 500 c.c.): the major portion dissolved, leaving a small residue of 8-nitro-1-naphthylamine. The combined extracts were neutralised with ammonia and the precipitated 5-nitro-1-naphthylamine (8 g.) was crystallised from ligroin, forming red plates, m. p. 119° (Found: N, 15·0. Calc.: N, 14·9%). The original filtrate was diluted with water to 500 c.c., filtered, and neutralised with ice-cold ammonia; the precipitated 8-nitro-1-naphthylamine crystallised from ligroin in bright red needles, m. p. 97° (Found: N, 15·0%). Total yield of this isomeride, 5 g.

(b) *With various amounts of nitric acid.* The above procedure was repeated with 8·8 g., 8·0 g., and 22 g. of potassium nitrate. The yields of 5-nitro- and 8-nitro-1-naphthylamine obtained are in the table.

Mononitration of β-*Naphthylamine.*—Four nitrations were carried out, as described above, with β-naphthylamine (14 g.) and 11 g., 8·8 g., 8·0 g., and 22 g. of potassium nitrate. The precipitated solid was the sulphate of 5-nitro-2-naphthylamine free from tar. The liberated base rystallised from glacial acetic acid in red needles, m. p. 143—144° (Found: N, 15·1%). The filtrate from the sulphate, when neutralised with ammonia, gave 8-nitro-2-naphthylamine, which crystallised from glacial acetic acid in red needles, m. p. 103—104° (Found: N, 15·0%). The yields are reported in the table.

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The Second Dissociation Constant of Barium Hydroxide. By CECIL W. DAVIES

KILDE (*Z. anorg. Chem.*, 1934, **218**, 113) has shown that calcium hydroxide is incompletely dissociated in aqueous solution; the dissociation constant for the process $CaOH^{\cdot} \rightleftharpoons Ca^{\cdot\cdot} + OH'$ has the value $K = 0{\cdot}031$ (Kilde, *loc. cit.*; Davies, J., 1938, 278). It seemed of interest to compare this value with those of other alkaline-earth hydroxides, and for barium hydroxide the activity measurements of Harned and Mason (*J. Amer. Chem. Soc.*, 1932, **54**, 1441) provide the necessary data. The activity coefficients found by these authors for dilute solutions at 25° are markedly lower than those for calcium and barium chlorides, and we can conclude that the process $BaOH^{\cdot} \rightleftharpoons Ba^{\cdot\cdot} + OH'$ does not go to completion. If α is the fraction of the intermediate ion dissociated, we have the following relationship between the measured stoicheiometric activity coefficient, γ, and the mean ionic activity coefficient, f: $4\gamma^3m^3 = a_{\pm}{}^3 = f^3\alpha(1 + \alpha)^2m^3$. Here m is the molar concentration, $a_{\pm}$ the mean ion activity, and $(1 + \alpha)m$ the concentration of hydroxyl ion. It follows that $f^3/\gamma^3 = 4/\alpha(1 + \alpha)^2$, and this equation can be solved, by successive approximations, for α on the assumption that f is given by the general equation recently published (J., 1938, 2094). The results of the calculations are given below. Cols. 1 and 2, taken from Harned and Mason's paper, show respectively the molar concentration and the authors' "smoothed" activity coefficient. Col. 3 gives the mean ionic activity coefficient, calculated from the equation $\log f = -\sqrt{I}/(1 + \sqrt{I}) + 0{\cdot}20I$, and Col. 4 the degree of dissociation of the barium hydroxide ion. I is the ionic strength, given by $I = (1 + 2\alpha)m$, and K, the second dissociation constant of barium hydroxide, is calculated from the equation $\log K = \log \alpha(1 + \alpha)m/(1 - \alpha) - 2\sqrt{I}/(1 + \sqrt{I}) + 0{\cdot}40I$.

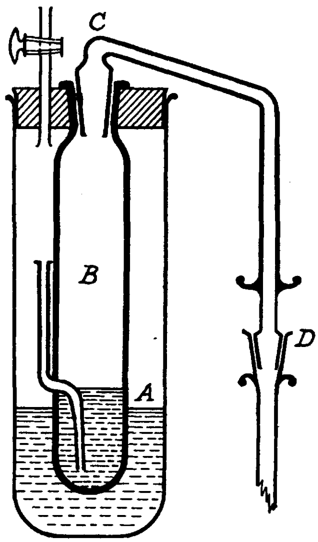
m.	γ.	f.	α.	I.	K.
0·009974	0·712	0·724	$0{\cdot}97_6$	0·02949	(0·41)
0·01505	0·661	0·685	$0{\cdot}94_5$	0·04349	$0{\cdot}23_6$
0·02010	0·627	0·657	$0{\cdot}93_0$	0·05750	$0{\cdot}22_3$
0·03070	0·579	0·616	$0{\cdot}90_9$	0·08650	$0{\cdot}22_3$
0·04074	0·549	0·589	$0{\cdot}89_8$	0·1139	$0{\cdot}23_6$
0·04990	0·526	0·571	$0{\cdot}88_3$	0·1380	$0{\cdot}23_2$
0·06151	0·502	0·553	$0{\cdot}86_2$	0·1676	$0{\cdot}22_0$

The constancy of K is good, and the value 0·23 can be accepted as the second dissociation constant of barium hydroxide. Thus calcium hydroxide is a far weaker electrolyte than barium hydroxide, and the evidence of the hydrolysis of magnesium salts suggests that magnesium hydroxide is weaker still.—BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, January 23rd,* 1939.]

A Micro-method for the Determination of the iso*Propylidene Group in Sugar Derivatives.* By

D. J. Bell and K. Harrison.

Elsner (*Ber.*, 1928, **61**, 2364) has described a procedure for the estimation of the *iso*propylidene group in sugar derivatives, which is inconvenient in that (*a*) a relatively large sample is required, and (*b*) it is necessary to distil the acetone in a stream of purified carbon dioxide. By the use of a compact steam-distillation apparatus designed by one of us (K. H.) in connection with another problem, these and other disadvantages are removed, and a sample giving 1 mg. of acetone may be analysed with an accuracy of ± 1%.



The apparatus consists of a boiler *A*, provided with a stop-cock to equalise pressures and prevent regurgitation at the end of a distillation; it is essential that broken tile be added to promote even boiling. Steam passes through the reaction mixture in *B*; the ground joint at *C* is lubricated with syrupy phosphoric acid, and that at *D* with water. The tube *CD* must be stoutly made, as it carries the weight of a condenser (attached by steel springs).

A glass capsule holding the material to be analysed (enough should be taken to yield 0·6—1·2 mg. of acetone) is dropped into 5 ml. of N-sulphuric acid previously placed in *B*; the condenser delivery-tube is caused to dip below the surface of a freshly prepared solution containing 25 ml. of N/100-iodine in 5 ml. of N-sodium hydroxide. After 20 minutes' boiling, the stop-cock is opened, the condenser disconnected and washed out, and after acidification with 7 ml. of N-sulphuric acid, the excess of iodine is titrated with N/100-sodium thiosulphate. A blank is run for each batch of determinations.

Typical Results.

Substance.	% Acetone.	
	Found.	Calc.
Diacetone glucose	44·8	44·6
3 : 4-Monoacetone β-methylgalactoside	25·7	24·8
3 : 4-Monoacetone 2 : 6-dimethyl β-methylgalactoside	21·9	22·1
3-Acetyl diacetone glucose	38·2	38·4
3 : 4-Monoacetone 2-methyl β-methylgalactoside 6-nitrate	20·6	19·7
3-*p*-Toluenesulphonyl diacetone glucose	28·4	28·2
β-Diacetone fructose	45·0	44·6
Potassium diacetone 2-ketogluconate monohydrate	34·7	35·1

In certain cases, where the substance is not soluble in water, decomposition can be effected by hydrolysis in N-sulphuric acid with 20% of tri- or tetra-methyl glucose added to promote solution. We have sought in vain for other effective solvents which are not volatile in steam; a large number of volatile compounds were examined, but all reacted with the alkaline hypoiodite. The method is not applicable directly to benzoyl or benzylidene derivatives; pentoses do not interfere.

The authors are indebted to Dr. Stanley Peat for certain of the substances investigated.—The Biochemical Laboratory, Cambridge. [*Received, January* 12*th*, 1939.]