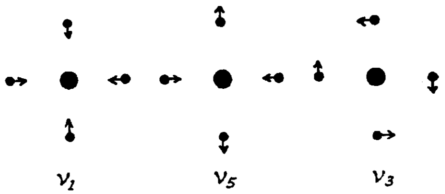
NOTES.

The Raman Spectrum of the [AuCl$_4$]$^-$ *Ion.* By J. D. S. Goulden, Allan Maccoll, and D. J. Millen.

A theoretical study of the vibrations of square molecules (Mathieu, *J. Chim. physique*, 1939, **36**, 271, 308; Maccoll, *J. Proc. Roy. Soc. N.S.W.*, 1944, **77**, 130) shows that three frequencies should be active in the Raman spectra of [AX$_4$]$^-$ ions. The modes of vibration are shown in the annexed diagram. Of the lines corresponding to these, the first will be polarised, and the last two depolarised. Further, the ν_1 and ν_5 frequencies will in the first approximation be identical, separation only occurring by virtue of cross terms in the potential function. Mathieu (*loc. cit.*) has examined the Raman spectra of the ions [Ni(CN)$_4$]$^{--}$, [Pd(CN)$_4$]$^{--}$, and [Pt(CN)$_4$]$^{--}$, but it is only for the last two that the spectra are in any way complete. The spectral study confirmed the planar structure of these ions.

Simple examples of square complexes are the ions [AuCl$_4$]$^-$ and [ICl$_4$]$^-$. These arise from the electronic configurations *dsp*^{2} and *d*^{2}*sp*^{3} respectively, the unshared pairs in the latter compound occupying the remaining two octahedral positions (Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1940).

Since solutions of " gold chloride," HAuCl$_4$,4H$_2$O are yellow, it was necessary to employ the Hg$_{5461}$-green line for excitation, as the solution absorbed light of shorter wave-lengths. A saturated aqueous solution of " gold chloride " was introduced into a small horn-shaped Raman tube of 4-c.c. capacity. Light from a single horizontal D.C. mercury arc was used as a source of exciting radiation, and the Hg$_{5461}$ line was isolated by passing the light through a 1-cm. layer of a saturated cupric chloride solution, and through a 1-cm. layer of a saturated neodymium trichloride–praseodymium trichloride solution. The second filter served to reduce the intensity of the Hg-yellow lines. The spectra were observed using an f4 Hilger spectrograph, the dispersion in the relevant region of the spectrum being about 150 A. per mm. The experimental arrangement of filters, cell, and reflectors has been described elsewhere (Goulden and Millen, *J.*, in the press). Exposures of about four days with a slit width of 0·2 mm. were required to produce a spectrum of suitable intensity. Previously prepared calibration tables were used for determining the frequencies.



A number of exposures were made, but even with the longest exposure only a single Raman frequency, at 370 ± 5 cm.$^{-1}$, appeared. A microphotometer trace showed a double peak at this frequency. Similar exposures with aqueous potassium tetrachloroperiodate solutions showed that this solution absorbed the Hg-green light too strongly to give a Raman spectrum.

The frequency 370 cm.$^{-1}$ of the aurichloride ion can reasonably be identified with the pair of frequencies ν_1, ν_5, which, as has been pointed out previously, will lie very close to one another. This is borne out by Mathieu's experiments with the platinicyanide ion, for which the observed frequencies were 455, 465 cm.$^{-1}$. The third frequency for aurichloride might be expected from Mathieu's results to lie at about 90 cm.$^{-1}$, in which position it would be obscured by the breadth of the exciting line. The observed spectrum of the aurichloride ion thus confirms the square structure.

The stretching force constant may be calculated from the observed frequency by means of

$$\nu_1 = \frac{1}{2\pi c}\left(\frac{k}{m}\right)^{1/2}$$

where k is the force constant of the Au–Cl bond and m is the mass of the chlorine atom (Maccoll, *loc. cit.*), leading to $k = 2{\cdot}86 \times 10^5$ dynes cm.$^{-1}$. This value is of the same order of magnitude as those for the ions $[Pd(CN)_4]^{--}$ and $[Pt(CN)_4]^{--}$ given by Mathieu, *viz:*

Ion.	(cm.$^{-1}$).	$k \times 10^{-5}$ (dynes cm.$^{-1}$).
$[Pd(CN)_4]^{--}$	439	2·93
$[Pt(CN)_4]^{--}$	465	3·30
$[AuCl_4]^{-}$	370	2·86

The authors express their appreciation of the interest shown by Professor C. K. Ingold, F.R.S., in this work.—SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON, W.C.1. [*Received, January 31st,* 1950.]

The Determination of Carbohydrate Residues in Pentose Nucleic Acids. By G. R. BARKER.

IN connection with work directed towards the examination of pentose nucleic acids from various tissues, it was necessary to have available a convenient method for the determination of the pentose nucleic acid content of materials obtained both for purposes of characterisation and as a guide in the extraction procedures. Analytical methods based on the determination either of heterocyclic bases or of phosphorus are inconvenient, because they do not distinguish between the pentose and the deoxypentose nucleic acids or because of their complexity. Colorimetric analysis for pentoses which are first converted into furfuraldehyde (for references see Davidson, *Cold Spring Harb. Symp. quant. Biol.*, 1947, **12**, 50) suffers from disadvantages. First, it is susceptible to interference from various materials not yielding furfuraldehyde and on this account is not applicable directly to crude nucleoproteins (Schneider, *J. Biol. Chem.*, 1945, **161**, 293). Secondly, the techniques so far described are liable to grave error in that only purine-bound pentose and not pyrimidine-bound pentose is normally converted into furfuraldehyde in anything approaching quantitative yield. Thus the apparent quantity of nucleic acid measured is dependent on the ratio of purine to pyrimidine nucleotides in the polynucleotide. It is assumed that this criticism applies also to the more recent method of Dische (*J. Biol. Chem.*, 1949, **181**, 379) since pyrimidine compounds are not discussed by him.

It has now been found that these difficulties are largely overcome by the use of Dunstan and Gillam's method (*J.*, 1949, S140). Since the programme of work in which this method is being used will not be complete for some time and the adaptation of the procedure for use in the nucleotide field has proved highly successful, the applicability of the method to the analysis of materials containing pentose nucleotides, together with necessary modifications in technique, are now briefly reported.

By use of the method as described, 100% recovery of ribose, computed from the spectroscopic measurement of furfuraldehyde, was obtained from adenosine, guanosine, yeast adenylic acid, and guanylic acid. With the pyrimidine nucleosides and nucleotides, although recoveries of ribose were higher than with other techniques, variable results were obtained unless the conditions of the steam-distillation were more rigidly controlled. Thus, for instance, if the rate of distillation was too rapid, the time occupied in collecting a reasonably convenient volume of distillate was insufficient for complete hydrolysis of the pyrimidine compounds which are very resistant to fission by acids : if, on the other hand, distillation was too slow, furfuraldehyde was not removed rapidly enough and underwent some decomposition, with a consequent low recovery. By distillation at a rate of approximately 5 c.c. per minute, maintained by a manostat controlling the burner of the steam generator, and collection of 110 c.c. of distillate, consistent results were obtained (see Table). Under these conditions, which may vary slightly with the dimensions of the apparatus and should be first found by experiment, recoveries of ribose from uridine, cytidine, and cytidylic acid were reproducible within the limits of accuracy of the method as stated by Dunstan and Gillam and were far nearer to the theoretical values than those obtained by other methods, which give results never above 50% of those expected and mostly far less :

Material.	Yield of furfuraldehyde, expressed as % recovery of ribose (mean value).	Material.	Yield of furfuraldehyde, expressed as % recovery of ribose (mean value).
Cytidine	93·9	Cytidylic acid	80·2
Uridine	90·8	Yeast nucleic acid...	88·5

Moreover, this method is simpler in operation than that of Massart and Hoste (*Biochim. Biophys. Acta*, 1947, **1**, 83) which is reported (Kerr, Seraidarian and Wargon, *J. Biol. Chem.*, 1949, **181**, 761) to give unreliable results under some conditions.

As a result of controlling the rate of flow of steam, it was found that the necessary distillation temperature was more easily maintained and the method was made semi-automatic in the following ways. First, a mercury thermostat was included in the distillation tube, and secondly, the distillation was stopped mechanically by placing the receiver on the pan of a rough balance which activated a tilting mercury switch controlling the gas supply both to the burner of the steam generator and to that beneath the distillation tube.

By this method it is possible to determine with reasonable certainty the number of carbohydrate residues in a polynucleotide without relying for calculation on a knowledge of the ratio of purine to pyrimidine nucleotides in the material under test. It is seen from the Table that the yield of furfuraldehyde from yeast ribonucleic acid is consistent with its formulation as a polynucleotide in which nitrogenous, carbohydrate, and phosphoric acid residues are present in equal numbers. The theoretical recovery of ribose is calculated for purposes of comparison for a tetranucleotide formed from the union of one molecule each of guanylic, adenylic, cytidylic, and uridylic acids.

Having established that the method is applicable to nucleic acids or their derivatives, it was tested next on protein-containing materials which are not suitable for analysis directly by most other methods. These fail either because of the formation of coloured compounds between the reagent used and materials other than furfuraldehyde or because of the production of furfuraldehyde from materials other than pentoses. The latter difficulty is inherent in any technique based on the determination of furfuraldehyde but it was considered possible that the former source of error would not affect the spectroscopic determination of furfuraldehyde, provided that the distillate did not contain other compounds exhibiting appreciable absorption at 278·5 mμ. To test this, the absorption of the steam-distillate from a crude nucleoprotein from beef pancreas was measured between 249 and 298 mμ. The absorption curve fitted exactly that obtained from a distillate from ribose itself and it is concluded that the distillate from the nucleoprotein contained no interfering substances. Furthermore, the protein part of the pancreas material, after being freed from nucleic acids by the method of Sevag, Lackman, and Smolens (*J. Biol. Chem.*, 1938, **124**, 425), gave a steam-distillate exhibiting no specific absorption in this region. Finally, the proportion of pentose nucleic acid present in the crude pancreas nucleoprotein, measured by the method of Schmidt and Thannhauser (*J. Biol. Chem.*, 1945, **161**, 83), was, within the limits of the accuracy of the two procedures, the same as that found by direct analysis for ribose by the modified technique here described.

It is considered, therefore, that providing suitable tests are applied as suggested above, the spectroscopic method for the determination of furfuraldehyde may be applied directly, not only to pentose nucleic acids, but also to nucleoproteins.—THE UNIVERSITY, MANCHESTER, 13. [*Received, March 2nd*, 1950.]

Ethylindole-, 5-Methylindole-, and 5-Methoxyindole-3-carboxylate : a Correction. By G. F. SMITH.

IN a recent publication (*Compt. rend.*, 1946, **222**, 1178), Mentzer claims to have obtained the compounds mentioned in the title by heating aniline, *p*-toluidine, and *p*-anisidine with ethyl formylchloroacetate. Repetition of this work has led to the formation of substances the melting points of which correspond to those of Mentzer's supposed indole-3-carboxylic esters, but which are now clearly identified as ethyl α-chloro-β-aryliminopropionates.

When the reaction between aniline and ethyl formylchloroacetate is carried out at room temperature, a compound of lower melting point is obtained. Since this compound has an ultra-violet absorption spectrum practically identical with that of Mentzer's product, m. p. 82°, has the same carbon and hydrogen content, and can be converted into it by distillation or by repeated crystallisation, it is concluded that the two compounds are geometrical isomers involving the carbon–nitrogen double bond.

Ethyl α-chloro-β-(*p*-methoxyphenylimino)propionate is recovered unchanged after being heated with pyridine or diethylaniline for 5 hours at 100°. The mother-liquors from the crystallisation of the recovered material give no colour on being heated with Ehrlich's reagent, indicating a total absence of indole compounds. Ring closure to an indole, together with very extensive decomposition, does, however, occur when α-chloro-β-(*p*-methoxyphenylimino)propionate is refluxed in diethylaniline for 30 minutes, for the amorphous acid fraction from the saponification of the ether-soluble portion of the reaction product gives a very strong purple colour with Ehrlich's reagent. No attempt has been made to isolate the methoxyindolecarboxylic acid.

Mentzer's claim was precariously based on (*a*) the assumption that, since ring closure to an indole occurs when an arylamine and an ω-bromoacetophenone are heated together, it will also occur when the reaction is carried out with an arylamine and ethyl formylchloroacetate, and (*b*) the nitrogen content of the product of interaction of *p*-toluidine and ethyl formylchloroacetate [Found, 6·2%. Calc. for ethyl 5-methylindole-3-carboxylate, 6·9%. Note that the value calculated for ethyl α-chloro-β-(*p*-tolylimino)-propionate is 5·85%].

Experimental.—*Ethyl α-chloro-β-phenyliminopropionate.* (*a*) Equivalent proportions of aniline and ethyl formylchloroacetate are heated together at 180° for 5 minutes, and the very dark product distilled *in vacuo*. The fraction, b. p. 175—182°/8 mm., crystallises completely, and the *ester* then separates from ethanol as colourless prisms and from light petroleum as colourless blades, m. p. 80—81° (Found : C, 58·7; H, 5·3; N, 6·45; Cl, 15·4. $C_{11}H_{12}O_2NCl$ requires C, 58·5; H, 5·35; N, 6·2; Cl, 15·7%). Mentzer (*loc. cit.*) gives m. p. 82°. (*b*) A solution of the reactants in ethanol is left for a few minutes at room temperature; crystallisation then occurs on scratching it. The *product* separates from light petroleum as colourless blades, m. p. 68—68·5° (sinters 67°), and from ethanol as colourless slender prisms, m. p. 69° (Found : C, 58·5; H, 5·7. $C_{11}H_{12}O_2NCl$ requires C, 58·5; H, 5·35%). A mixture of high- and low-melting compounds melts at 79—81° (sinters 70°). The same mixture, m. p. 76—79·5°, is obtained when either the high- or the low-melting form is fused and allowed to resolidify. Repeated crystallisation of the low-melting form results in the gradual rise of the melting point to 80—81°.

Ultra-violet absorption spectra.	$\lambda_{max.}$	Inflexion.
Isomer, m. p. 80—81°	316·5 (ε, 29,580)	293 mμ. (ε, 16,030)
Isomer, m. p. 69°	315·5 (ε, 29,850)	293 mμ. (ε, 16,260)

Ethyl α-chloro-β-(p-*tolylimino*)*propionate.* Equivalent proportions of *p*-toluidine and ethyl formylchloroacetate react exothermally, and crystallisation occurs on scratching the product. The *ester* is drained by suction and thrice crystallised from ethanol, from which it separates as slender monoclinic prisms, m. p. 95·5—96° (Found : C, 60·3; H, 6·25; Cl, 15·1. $C_{12}H_{14}O_2NCl$ requires C, 60·1; H, 5·9; Cl, 14·8%). Mentzer (*loc. cit.*) gives m. p. 97°.

Ethyl α-*chloro*-β-(p-*methoxyphenylimino*)*propionate.* This *compound,* prepared as above from *p*-anisidine and ethyl formylchloroacetate, separates from ethanol as colourless stout tetragonal crystals, m. p. 96—96·5° (Found : C, 56·4; H, 5·8; Cl, 14·2. $C_{12}H_{14}O_3NCl$ requires C, 56·35; H, 5·5; Cl, 13·85%). Mentzer (*loc. cit.*) gives m. p. 97°.

The author expresses his thanks to Dr. H. T. Openshaw for his help and advice.—UNITED COLLEGE, UNIVERSITY OF ST. ANDREWS; THE UNIVERSITY, MANCHESTER. [*Received, March* 6*th*, 1950.]

A Heterocyclic Perfluoro-compound. By R. N. HASZELDINE.

THE complete fluorination of hydrocarbons has been achieved using the catalytic, the cobalt trifluoride, and the electrochemical method. In the first, fluorine and the hydrocarbon interact on the surface of a gold- (Haszeldine and Smith, *J.*, in the press) or a silver-plated (Cady, Grosse *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 290) copper catalyst; the second method utilises the fact that cobalt trifluoride, when heated, reacts with a hydrocarbon vapour to replace hydrogen by fluorine and to saturate double bonds by fluorine (Fowler *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 292; Haszeldine and Smith, forthcoming communication); the third method involves electrolysis of a solution of the hydrocarbon in anhydrous hydrogen fluoride (Simons, *J. Electrochem. Soc.*, 1949, 47).

The fluorination of compounds containing nitrogen has received little attention : the electrolysis of pyridine in anhydrous hydrogen fluoride (Simons, *loc. cit.*) yields nitrogen trifluoride and perfluoropentane, and not perfluoropiperidine; Ruff and Giese (*Ber.*, 1936, **69**, 604) have claimed that several isomeric compounds $C_2N_2F_6$, which include two compounds with four-membered heterocyclic ring systems, result from the interaction of fluorine and silver cyanide. The complete fluorination of a heterocyclic nitrogen-containing compound has not yet been reported.

The fluorination of 2 : 6-lutidine has now been investigated. The catalytic and cobalt fluoride methods were used successfully after slight modification to prevent, as far as possible, the formation of the non-volatile hydrofluoride of the dimethylpyridine. A product believed to be *perfluoro*-2 : 6-*dimethylpiperidine* has been isolated as a solid, m. p. 94—95° [Found : C, 22·1; N, 3·5; *M* (ebullioscopic), 370. $C_7F_{15}N$ requires C, 21·9; N, 3·7%; *M*, 383], with a characteristic musty odour, which can be purified by sublimation at 50—60°/760 mm. or by recrystallisation from carbon tetrachloride. Perfluoro-2 : 6-dimethylpiperidine crystallises as large needles and is readily soluble in hot carbon tetrachloride but much less soluble at room temperature; in this respect it resembles perfluorohexadecane, $C_{16}F_{34}$, which, however, crystallises as plates from carbon tetrachloride (Haszeldine and Smith, forthcoming communication).

It is believed that the low yield (*ca.* 5%) of perfluoro-2 : 6-dimethylpiperidine is caused by formation and subsequent decomposition by fluorination of the hydrofluorides of lutidine and of compounds derived from lutidine by the introduction of one or two atoms of fluorine. Once a certain degree of fluorination has been achieved, however, the basicity of the nitrogen-containing compound is so reduced that hydrofluoride formation cannot occur. Perfluoro-2 : 6-dimethylpiperidine does not give a precipitate with thorium nitrate solution.

The bulk of the product boils below room temperature and this volatile material is believed to contain fluorocarbons, nitrogenous compounds such as $CF_3{\cdot}NF_2$ and $(CF_3)_2NF$, and possibly nitrogen trifluoride, formed by disruption of the ring.—UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, March* 9*th*, 1950.]

The Condensation of Pyrrole-2-aldehyde and Hydantoin. By D. G. HARVEY.

5-(2-PYRRYLMETHYLIDENE)HYDANTOIN has been envisaged as an intermediate in the synthesis of 2-pyrryl-β-alanine by Herz and Dittmer (*J. Amer. Chem. Soc.*, 1948, **70**, 503) although they were unable to effect the necessary condensation of pyrrole-2-aldehyde and hydantoin in ethanol with catalytic quantities of piperidine. By use of purified reactants and strict adherence to a given time of heating a crystalline compound has now been isolated which gives analytical figures suggesting that it is 5-(2-*pyrrylmethylidene*)-*hydantoin*. So far all attempts to produce the reduced hydantoin by standard methods have been unsuccessful.

Pyrrol-2-aldehyde, (2·0 g.; prepared according to Fischer and Orth, "Die Chemie des Pyrrols," Vol. I, 1934, p. 152, and purified by two recrystallisations), hydantoin (2·4 g.), redistilled piperidine (2 ml.), and absolute ethanol (20 ml.; distilled over sodium) were boiled under reflux for 1 hour. After removal of most of the solvent *in vacuo*, and acidification to litmus by dilute acetic acid (10% v/v) a yellow crystalline solid separated (2·5 g., 73%). It was recrystallised with some difficulty from aqueous-ethanolic pyridine (1 : 1 : 1) in yellowish-brown needles, m. p. 228—230° (Found : C, 54·0; H, 4·07; N, 23·2. $C_8H_7N_3O_2$ requires C, 54·2; H, 3·95; N, 23·7%. Analysis by Drs. Weiler and Strauss, Oxford).

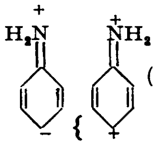
The work was performed in the Department of Physiology, Royal Veterinary College.—DEPARTMENT FOR RESEARCH IN INDUSTRIAL MEDICINE, M.R.C. LABORATORIES, HAMPSTEAD, LONDON, N.W.3. [*Received, March* 10*th*, 1950.]

Mechanism of the Benzidine Rearrangement. By E. D. HUGHES and C. K. INGOLD.

THIS subject has been discussed by Ingold and Kidd (*J.*, 1933, 954), and Hughes and Ingold (*J.*, 1941, 608), who assumed conjugative electron displacements from *p*- to *p'*-positions in an intermediate state of the formation of the univalent cation (I); by Robinson (*J.*, 1941, 220), who postulated similar displacements (not reversed, as Dewar has stated) in fully-formed (I); and also by Hammick and Mason (*J.*, 1946, 638), who interrupted the conjugation in order to include an extra angle in the structure (but not a boat-shaped ring, as Dewar has asserted), thus bringing the *pp'*-positions nearer; and finally by Dewar (*J.*, **1946**, 406, 777; *Disc. Faraday Soc.*, **1947**, **2**, 50; "Electronic Theory of Organic Chemistry," Oxford, **1949**, p. 235), who transfers the charge in (I) to the neighbouring ring, which he then allows to take in electrons from the other ring, thus establishing a "π-bond."

(I.) $\mathrm{Ph\overset{+}{N}H_2{\cdot}NHPh}$ $\mathrm{Ph\overset{+}{N}H_2{\cdot}\overset{+}{N}H_2Ph}$ (II.)

Hammond and Shine (*J. Amer. Chem. Soc.*, 1950, **72**, 220) have recently adduced evidence that the rearranging entity is the bivalent cation (II), a finding which seems to us to allow a solution of all the main difficulties. The original difficulty, which made Kidd, Hughes, and Ingold refuse to contemplate fully-formed (I) as the rearranging entity, *viz.*, that of moving electrons from a positive nitrogen atom to a neutral one, is overcome by making the second nitrogen atom positive. Then, (II) has adjacent charges, which can plausibly be supposed so to weaken the N–N-link that its electrons can functionally conjugate (or "hyperconjugate") with the aromatic π-electrons, thereby completing the internuclear conducting system. This could enable near-integral charges to be built up in the *pp'*-positions; and, even though the minimum separation of these positions would be about 4·2 A. in strainless (II), this is not too great a distance for the establishment in (III) of a fairly strong electrostatic (or mainly electrostatic) bond; which, as the unlike charges come together and the like charges separate, would smoothly go over into a covalency in the product of the rearrangement.—UNIVERSITY COLLEGE, LONDON, W.C.1. [*Received, March* 31*st*, 1950.]



(III.)