NOTES.

Dipole Moment and Structure of Organic Compounds. Part XIV. The Direction of the Electric Moment of the N⋮C *Group.* By A. WEISSBERGER and R. SÄNGEWALD.

IT has been stated that 4 : 4′-dicyanodiphenyl has an electric moment of 1·1*D* (*Helv. Phys. Acta*, 1929, **2**, 257), and from this result the deduction has been made that the N⋮C group is without axial symmetry, *i.e.*, that the direction of its moment does not coincide with the bond joining this group to the benzene ring. The fact that the electric moments of certain aromatic nitriles experimentally determined do not agree with the values which would be predicted by a simple vector addition of the component moments has been considered evidence in support of the same conclusion (*Z. physikal. Chem.*, 1930, *B*, **10**, 397), although this lack of agreement may well arise from polarisation effects in the attached groups or in the nucleus (*Proc. Roy. Soc.*, 1933, **140**, 562; *Z. physikal. Chem.*, 1933, *B*, **20**, 151; *Trans. Faraday Soc.*, 1934, **30**, 884).

We thank Dr. C. G. Hampson for an attempt to redetermine the electric moment of 4 : 4′-dicyanodiphenyl. This, however, was not possible because of the low solubility of the compound in benzene at 25° and in decalin at 70°. However, *p*-dicyanobenzene was just soluble enough to be measured in the usual way with benzene as solvent, and the moment has been found to be indistinguishable from zero. It thus appears that the cyano-group shows axial symmetry in accordance with the ordinary model. It would be without analogy if a 4 : 4′-derivative of diphenyl had a moment whilst the *p*-benzene derivative had none. No details on the measurement of the diphenyl compound have been given, and hence it is difficult to suggest the origin of the discrepancy between the earlier result and ours.

p-Dicyanobenzene was prepared according to Limpricht (*Annalen*, 1876, **180**, 89) and recrystallised from alcohol; m. p. 222°. 4 : 4′-Dicyanodiphenyl was prepared according to Ferris and Turner (J., 1920, **117**, 1149). The crude product was sublimed at 190°/0·002 mm. and recrystallised from dioxan and from benzene; m. p. 235—236°.

p-Dicyanobenzene in Benzene (25·0° ± 0·1°).

f_2, %.	$d^{25°}_{4°}$.	ϵ.	n^2.	$P_{1,2}$.	$P_{1,2}''$.
0	0·8735	2·272	2·2443	26·610	26·194
0·3780	0·8743	2·274	2·2452	26·672	26·249
0·5183	0·8749	2·275	2·2460	26·696	26·267
0·6625	0·8752	2·277	2·2464	26·726	26·287

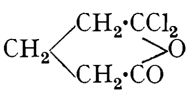
$dP_{1,2}/df_2 = 16{\cdot}9$; $dP_{1,2}''/df_2 = 14{\cdot}2$; $P_2 = 43{\cdot}5, P_2'' = 40{\cdot}4$.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, March 8th*, 1935.]

The Structure of Tolan. By ARNOLD WEISSBERGER.

SMYTH and DORNTE (*J. Amer. Chem. Soc.*, 1931, **53**, 1296) found for tolan an electric moment of 1·12 *D* and therefore suggested the formula $(C_6H_5)_2C{\vdots}C$. Weissberger and Sängewald (*Z. physikal. Chem.*, 1933, *B*, **20**, 145), however, stated that the moment of tolan, measured in the usual way, is indistinguishable from zero, and therefore no reason exists to abandon the symmetrical formula established by organic chemists. Berger (*Z. physikal. Chem.*, 1935, *B*, **28**, 95), as a result of measurements of and deductions from association phenomena, decides in favour of the asymmetrical formula in spite of the absence of a moment. He points out that this may be small, because the moment of *as.*-diphenylethylene is very small (0·5 *D*). I cannot agree with this argument. In the circumstances, however, it seemed worth while to provide *chemical* evidence for one or the other formula. The usual methods of preparation of tolan from *s.*-diphenylethane derivatives are with some reason not considered definite proof, because they may involve rearrangements which are frequent in this group of compounds. However, catalytic reduction of tolan at room temperature can hardly involve a rearrangement of the skeleton. This has been carried out by Kelber and Schwarz (*Ber.*, 1912, **45**, 1951), dibenzyl being obtained after recrystallisation of the product. Unfortunately the authors state no yield. Their method of reduction was therefore repeated with 0·445 g. of tolan. After 2 hours, the theoretical amount of hydrogen had been absorbed; the solution (acetic acid) was filtered and poured into water and the crystals were collected. The yield was 0·442 g. (99·3% of the theo.) of dibenzyl, m. p. 52·5—53·2°. As *as.*-dibenzylethane is liquid at room temperature, this should be considered definite proof for the symmetrical formula of tolan.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, March* 22*nd*, 1935.]

The Structure of Glutaryl Chloride. By S. G. P. PLANT and (Miss) M. E. TOMLINSON.

SUBSTANCES hitherto obtained from glutaryl chloride have been derived from its symmetrical form, although the unsymmetrical structure (I) might be responsible for the formation from chlorobenzene of an ill-defined product described by Skraup and Guggenheimer (*Ber.*, 1925, **58**, 2488). It has now been found that both forms are involved in the reaction with anisole and aluminium chloride, the resulting isomeric *αγ-dianisoylpropane* and *δδ-di-*p*-anisylvalerolactone* being separated by extracting the latter with aqueous sodium carbonate. Two similarly constituted ethoxy-compounds have been obtained from phenetole, and *γ-anisoyl-* and *γ-phenetoyl-butyric acid* have been prepared for comparison from anisole and phenetole respectively with glutaric anhydride.


(I.)

αγ-Dianisoylpropane and its Isomeric Lactone.—A mixture of anisole (14·6 g.), glutaryl chloride (9·3 g.), and carbon disulphide (30 c.c.) was treated with pulverised aluminium chloride (12 g.) and refluxed for 2 hours. After the solvent had been allowed to evaporate, the residue was treated with dilute hydrochloric acid, and any anisole removed in steam. When the sticky residual solid was warmed with aqueous sodium carbonate, *αγ-dianisoylpropane*, colourless needles (3·9 g.), m. p. 99°, from alcohol, remained (Found : C, 73·2; H, 6·4. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·4%), and from the filtered solution dilute hydrochloric acid precipitated *δδ-di-*p*-anisylvalerolactone* as a sticky mass. It was purified by distillation under reduced pressure and obtained from benzene–petroleum in colourless prisms (3·1 g.), m. p. 111—113° (Found : C, 73·1; H, 6·6%).

By a similar process from phenetole, *αγ-diphenetoylpropane*, colourless needles, m. p. 133°, from alcohol (Found : C, 74·1; H, 7·3. $C_{21}H_{24}O_4$ requires C, 74·1; H, 7·1%), and *δδ-di-*p*-phenetylvalerolactone*, colourless prisms, m. p. 82°, from benzene–petroleum (Found: C, 73·8; H, 6·9%), were obtained. Both lactones were readily dissolved by cold aqueous sodium carbonate.

γ-Anisoyl- and γ-Phenetoyl-butyric Acid.—When glutaric anhydride was allowed to react with anisole under conditions similar to those described above, the product, after removal of the volatile material in steam, was entirely soluble in aqueous sodium carbonate. *γ-Anisoylbutyric acid*, practically colourless prisms, m. p. 137°, from alcohol, was then precipitated from the solution by the addition of hydrochloric acid (Found : C, 65·1; H, 6·3. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%). Prepared similarly from phenetole, *γ-phenetoylbutyric acid* separated from benzene in almost colourless prisms, m. p. 114° (Found : C, 66·2; H, 6·6. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%).

The authors are grateful to the Chemical Society for a grant.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, May* 11*th*, 1935.]

2-*Iodo*-3-*Hydroxybenzoic Acid.* By THOMAS A. HENRY and THOMAS M. SHARP.

SOME years ago the authors described an iodo-3-hydroxybenzaldehyde in which the position of the iodine was uncertain (J., 1922, **121**, 1059). This aldehyde on oxidation with permanganate in acetone yielded a minute amount of a substance, m. p. 133° (in error this was given as 233° in the paper), which was assumed to be the corresponding iodo-3-hydroxybenzoic acid. It was subsequently shown by two other methods (J., 1924, **125**, 1051) that the aldehyde in question was 2-iodo-3-hydroxybenzaldehyde, so the substance produced on oxidation should have been 2-iodo-3-hydroxybenzoic acid. As this acid would be expected to have a higher melting point than 133°, and there are numerous instances on record of failure to oxidise aromatic hydroxyaldehydes to the corresponding acids (*e.g.*, Tiemann, *Ber.*, 1876, **9**, 415; Brady and Dunn, J., 1915, **107**, 1859), the authors have thought it advisable to repeat the previous observation and to effect the oxidation by another method.

Repetition of the direct oxidation of 2-iodo-3-hydroxybenzaldehyde with permanganate in acetone gave again a minute yield of crystalline substance, m. p. about 133°, which has proved to be merely impure recovered aldehyde (m. p. 159—160°), and no acid could be isolated. The required acid has now been obtained in small, though sufficient yield, by oxidation of the acetyl derivative of the aldehyde, followed by hydrolysis.

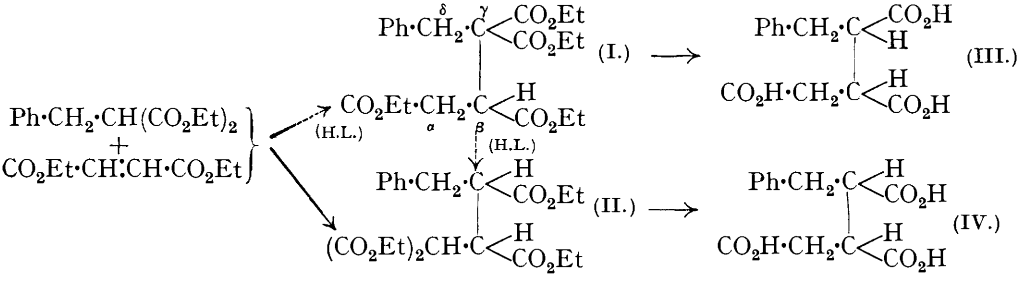
2-Iodo-3-hydroxybenzaldehyde (2 g.) was boiled for 1 hour with acetic anhydride (10 c.c.), and the excess of reagent removed under reduced pressure. The oily acetyl derivative was dissolved in acetone (25 c.c.) and treated with potassium permanganate (2·4 g.), added in small quantities. The solution quickly became decolorised: the manganese dioxide was filtered off, suspended in water, and decomposed with sulphur dioxide. This furnished a small amount of acid (0·4 g.). The acetone filtrate on evaporation left an oil, which was extracted with 5% sodium bicarbonate solution. The alkaline solution, after acidification, yielded to ether a further quantity of acid (0·41 g.), whilst unoxidised aldehyde remained undissolved by the bicarbonate. This portion was again oxidised with permanganate in the same manner, and the unoxidised portion treated similarly a third time. In this way there were finally obtained 1·27 g. of 2-*iodo*-3-*acetoxybenzoic acid*, which crystallised from benzene in colourless needles, m. p. 179—180° (corr.) (Found: C, 35·55; H, 2·4; I, 41·5. $C_9H_7O_4I$ requires C, 35·3; H, 2·3; I, 41·5%). On hydrolysis with 5% alcoholic potassium hydroxide, the acetylated acid was converted into 2-*iodo*-3-*hydroxybenzoic acid*, which formed colourless needles from chloroform, m. p. 158—159° (corr.) (Found: C, 31·9; H, 1·9; I, 48·2. $C_7H_5O_3I$ requires C, 31·8; H, 1·9; I, 48·1%). The melting point was depressed to 135° on admixture with 2-iodo-3-hydroxybenzaldehyde. It is noteworthy that the m. p. of the acetyl derivative is higher than that of the free hydroxy-acid, whereas the m. p.'s of the other two known iodo-*m*-hydroxybenzoic acids are higher than those of the corresponding acetyl derivatives (3-hydroxy-4-iodobenzoic acid, m. p. 226°, acetyl derivative, m. p. 203°; 3-hydroxy-6-iodobenzoic acid, m. p. 198°, acetyl derivative, m. p. 157°. Brenans and Prost, *Compt. rend.*, 1924, **178**, 1285).—Wellcome Chemical Research Laboratories, London, N.W.1. [*Received, April 11th*, 1935.]

Validity of Holden and Lapworth's Theory of the Mechanism of Abnormal Michael Additions.

By C. K. Ingold and H. N. Rydon.

Michael and Ross, reviving an early idea due to Thorpe, advanced the view that sodioalkylmalonic esters may undergo partition in the sense $R{-}\vdots{-}CNa(CO_2Et)_2$ during addition to unsaturated esters in the presence of an equivalent of sodium ethoxide (*J. Amer. Chem. Soc.*, 1930, **52**, 4600). Holden and Lapworth pointed out that this unorthodox assumption is unnecessary, and that every such apparent partition can be explained as a normal addition, followed by a change of structure due to Claisen condensation and alcoholysis (J., 1931, 2370).

Very recently one of us (H. N. R.) recommended a return to the hypothesis of Michael and Ross, on the ground (this vol., p. 420) that the actual product (shown to be II) from ethyl sodiobenzylmalonate and ethyl fumarate, and the normal addition product (I) (which can be prepared in an independent way) yield stereoisomeric, rather than identical, acids on hydrolysis (Duff and Ingold, J., 1934, 87). It is argued that different acids (III and IV), having two asymmetric carbon atoms (β and γ), cannot both be formed through a single ester (I), having only one (β), as Holden and Lapworth's mechanism requires.



(⟶ observed transformations. $\overset{(H.L.)}{\dashrightarrow}$ Holden and Lapworth's theory.)

The writers desire to point out the following. The two γ-carbethoxyl groups of (I) are distinguishable inasmuch as, when the chain $\alpha\beta\gamma\delta$ is coplanar, one is "*cis*-" and the other "*trans*-" with respect to the β-carbethoxyl group. If the changes (I) ⟶ (III) and (I) ⟶ (II) involve the loss or displacement of different γ-carbethoxyl groups, and the numbers of Walden inversions in the two changes are equal (both one, or both zero), then the final acids will be stereoisomeric. Alternatively, if the two changes involve the same carbethoxyl group, but the numbers of Walden inversions differ by unity, then the final acids will still be stereoisomeric. There are thus various ways in which the observations can be accommodated to Holden and Lapworth's theory, which appears to be still acceptable.—UNIVERSITY COLLEGE, LONDON, W.C.1, and IMPERIAL COLLEGE, LONDON, S.W.7. [*Received, May 2nd,* 1935.]