352. *Notes on the Dipole Moments of* (a) 4 : 4′-*Dinitro- and* 4 : 4′-*Di-cyano-diphenyls, and* (b) *the Isomeric Diphenyl-*4 : 4′-*bisdiazocyanides.*

By R. J. W. LE FÈVRE and H. VINE.

(a) The apparent moments in benzene solution of 4 : 4′-dinitro- and -dicyano-diphenyl are $1·0_2$ and $1·3_0$ D. respectively; these results must be viewed as " anomalous," since the molecules both have axial symmetry.

(b) The two forms of diphenyl-4 : 4'-bisdiazocyanide (Euler, 1907) are shown by dipole-moment determination to be geometrical isomerides, the less stable modification being either the *cis-cis-* (I) or the *trans-cis-*form (II). The formation of the more stable variety from the less stable has been followed by dielectric-constant measurement and appears to be unimolecular.

THE measurements recorded in the two sections of this paper bear respectively on (a) the question of anomalous moments (cf. " Dipole Moments," Methuen, 1938, p. 93), and (b) the relative configurations of labile and stable diazocyanides. The two sections are not unrelated, since the unexpected possession of apparent polarity by the dicyano- and dinitro-diphenyls precludes any *a priori* estimates of the moments of the isomeric bisdiazocyanides being reasonably made.

(a) 4 : 4'-*Dicyano- and* 4 : 4'-*Dinitro-diphenyls.*—From previous measurements of polarisations and refractions of certain 4 : 4'-disubstituted diphenyl compounds in benzene solution non-polarity has been inferred, either by the observers themselves or by reviewers, and the conclusion drawn that the molecules concerned are collinear. Strictly, however, several of these determinations contain uncertainties, and do not permit the quotation of results more precisely than " less than *ca.* 0·4 D." The " apparent moments " reported for 4 : 4'-dicyano- and -dinitro-diphenyls stand apart from the others by reason of their magnitudes, which must have been due to something more than these ordinary errors.

For the dicyano-compound the possibility was mooted (Bretscher, *Helv. Physica Acta*, 1929, **2**, 257) that the ·C≡N group is without axial symmetry, but Weissberger and Sängewald (J., 1935, 855), having since examined 1 : 4-dicyanobenzene in benzene solution (finding $_TP_\infty$ 43·5 c.c. and $[R_L]_D$ 40·4 c.c.) have concluded that this is not so. Other explanations have been advanced (Bergmann, Engel, and Sandor, *Z. physikal. Chem.*, 1930, *B*, **10**, 397 ; *ibid.*, 1933, *B*, **20**, 151 ; Hampson and Sutton, *Proc. Roy. Soc.*, 1933, **140**, 562 ; Weissberger, Sängewald, and Hampson, *Trans. Faraday Soc.*, 1934, **30**, 844).

For the dinitro-compound, possibly owing to its sparing solubility, the earlier measurements are in disagreement among themselves [Williams (*J. Amer. Chem. Soc.*, 1928, **50**, 2350 ; *Physikal. Z.*, 1928, **29**, 271, 683) appears to have examined one solution only]. The result of Weissberger and Williams (*Z. physikal. Chem.*, 1929, *B*, **3**, 367) gives a *smaller* excess of total polarisation over refraction than is found in the case of 1 : 4-dinitrobenzene, for which the corresponding difference is *ca.* 7 c.c. (Le Fèvre and Le Fèvre, J., 1935, 957).

Present knowledge of " anomalous moments " of symmetrical molecules with equal but opposed polar groups suggested the desirability of repeating the measurements on both dicyano- and dinitro-diphenyls. This has now been done, and the apparent moments found as follow :

4 : 4'-Dicyanodiphenyl .... $(\mu)_{apparent} = 1\cdot3_0$ D.
4 : 4'-Dinitrodiphenyl .... $(\mu)_{apparent} = 1\cdot0_2$ D.

These " moments " are definitely larger than those of analogously substituted benzenes, as is the case with several other similarly related pairs for which data are recorded in the literature. Such an order could be forecast qualitatively, whether these anomalous " moments " were due either to the flexibility of the solute molecules under solvent bombardment (because if, *e.g.*, 1 : 4-dinitrobenzene were so distorted, 4 : 4'-dinitrodiphenyl would be likely to be more so) or to the possession by the solutes of abnormally large atomic polarisations (which, being roughly additive, would be greater for a larger molecule than for a smaller). This point is not clearly forecast by the quantitative treatments of anomalous solvent effects given recently by Jenkins (J., 1936, 862), Bauer (*J. Chem. Physics*, 1936, **4**, 458), and Frank and Sutton (*Trans. Faraday Soc.*, 1937, **33**, 1307) : the first two ignore altogether the *dimensions* of the solute molecule, and the last workers introduce only the cross-sectional area, which is presumably the same for a 1 : 4-disubstituted benzene as for a 4 : 4'-disubstituted diphenyl. Nevertheless, the possibility achieves a high *a priori* likelihood from the latest discussion by Coop and Sutton (this vol., p. 1269), in which it is considered that polar links, inversely with the rigidity with which they are held in the molecular structure, can originate in the measuring electric

field a real atomic polarisation. It is obvious that a 1 : 4-disubstituted benzene will be qualitatively less easily bent along the 1 : 4-axis than will a 4 : 4'-disubstituted diphenyl along the 4 : 4'-axis, in agreement with the experimental values cited above.

Note on a Previous Paper.—We have discussed (this vol., p. 967) the significance of the changes of total polarisation caused by the insertion into the 4 : 4'-positions of some 2 : 2'-disubstituted diphenyl compounds of two radicals whose " group moments " lie along their directions of attachment to the aromatic carbon atoms; *e.g.*, the polarisation of 2 : 2'-dinitrophenyl is 623 c.c., but that of 2 : 4 : 2' : 4'-tetranitrodiphenyl is 153 c.c. less, *viz.*, 470 c.c. The measurements now recorded suggest that " anomalous " polarisation effects would not have accounted for more than 22 c.c. so the change in this—as in the other instances—probably arose from a different cause.

Preparations and Measurements.—4 : 4'-*Dicyanodiphenyl.* This was prepared by a Sandmeyer reaction upon benzidine (Ferriss and Turner, J., 1920, **117**, 1140), and purified by extraction with alcohol, crystallisation successively from pyridine, acetic acid, and pyridine, followed by sublimation, and recrystallisation from alcohol; it formed thin needles, m. p. 230—238° (Doebner, *Annalen*, 1874, **172**, 116, and Ferriss and Turner quote m. p. 234°).

The following measurements are recorded under symbols which are explained in previous papers (*e.g.*, J., 1937, 1805); the mean values of $\alpha\varepsilon_2$ and βd_2 are calculated as the quotients $\Sigma(\varepsilon_{12} - \varepsilon_2)/\Sigma(w_1)$ and $\Sigma(d_{12} - d_2)/\Sigma(w_1)$ respectively.

| $100w_1$	0	0·4860	0·8917	0·9629
$\varepsilon_{1200}^{25°}$	2·2725	2·2780	2·2829	2·2835
$d_{40}^{25°}$	0·87378	0·87489	0·87584	0·87603

Whence mean $\alpha\varepsilon_2 = 1·15$, mean $\beta = 0·265$, and $_TP_\infty = 97$ c.c.; with $[R_L]_D = [2 \times$ (benzonitrile) $- 2H] = 62$ c.c., $_OP_{apparent} = 35$ c.c.

4 : 4'-*Dinitrodiphenyl.* This was obtained by direct nitration of diphenyl; it crystallised from alcohol as needles, m. p. 237—238°.

$100w_1$	0	0·0714	0·0806	0·0917	0·1172	0·1454
$\varepsilon_{1200}^{25°}$	2·2725	2·2729	2·2731	2·2733	2·2735	2·2735
$d_{40}^{25°}$	0·87378	0·87398	0·87396	0·87410	0·87421	0·87425

Whence mean $\alpha\varepsilon_2 = 0·75$, mean $\beta = 0·362$, and $_TP_\infty = 87·5$ c.c.; with $[R_L]_D$ as 66 c.c. (the found value for 2 : 2'-dinitrodiphenyl, cf. this vol., p. 967), $_OP_{apparent} = 21·5$ c.c.

(b) *The Isomeric Diphenyl-4 : 4'-bisdiazocyanides.*—We have already (this vol., p. 431) examined a number of the pairs of isomeric diazocyanides, discovered by Hantzsch, and shown that their dipole moments support the accepted formulations. For diphenyl-4 : 4'-bisdiazocyanide three structures are possible (I, II, III). Two forms have been
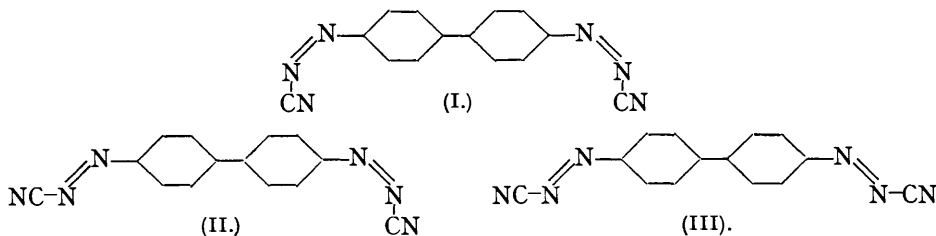

described by Euler (*Chem. Zentr.*, 1907, **78**, Part I, Vol. II, 1573), one decomposing at 98—100° and changing slowly in chloroform solution to a more stable form with a constant exploding point of 180°.

Prediction of the dipole moments to be expected for the above three molecules is made difficult by the possibility of (a) rotation of the polar —N:N—CN units about the axes joining them to the diphenyl skeleton and (b) the occurrence of anomalous solvent or atomic polarisation effects, such as those found for the related dinitro- and dicyanodiphenyls. However, their relative magnitudes are clear : in the infinitudes of configuration which may occur during rotation, only (I) and (III) can become centrosymmetric and there-

fore non-polar. Of these two, the *trans-trans*-form (III) has the N—CN groups oppositely directed, so the resultant group moments must nearly cancel; the *cis-cis*-form (I), on the other hand, has two considerable vectors in rotation. In cases like this the moment actually observed is an average of all the instantaneous molecular resultants (roughly given for examples of the present type by $\mu_{obs.} = \sqrt{2}\,\mu \sin\theta$, where two vectors of value μ are rotating at an angle $\theta°$ to an axis joining the points in space with which they are associated), and for (I), where θ is *ca.* 90° and μ *ca.* 3 D., this will definitely be higher than for (III), where θ and μ will be both quite small. The structure shown in (II) is also likely to correspond to a large moment, possibly even greater than that of (I).

In our experiments the more stable form has been obtained with a higher decomposition point (208°) than that recorded by Euler. Dipole-moment determinations have been carried out on both the modifications. These show that the less stable variety is either (I) or (II), while the more stable is probably (III). Preparations with the lower decomposition point had moments of 2·9 D. when first dissolved in benzene, but this value decreased steadily on keeping, finally approaching 1·8 D. This is taken as the moment of the more stable form. The spontaneous isomerisation was followed by dielectric-constant observations and appeared to obey a unimolecular law (time of half-change, about 35 hours at 25°); the interpretation of this, however, is complicated by the uncertainty as to the nature of the less stable bisdiazocyanide—it might consist of either (I) or (II), or a mixture of both. With the two solutions examined, crystallisation occurred suddenly after about 120 hours at 25°. The stable form so produced was too insoluble for dipole-moment measurements, and the density and dielectric-constant figures recorded on p. 1882 for this form are therefore values extrapolated from the velocity experiments.

Preparation and Measurements.—" AnalaR " Benzidine (10 g.) was dissolved in hot alcohol (80 c.c.), and 10N-hydrochloric acid (34 c.c.) added. The dihydrochloride which separated
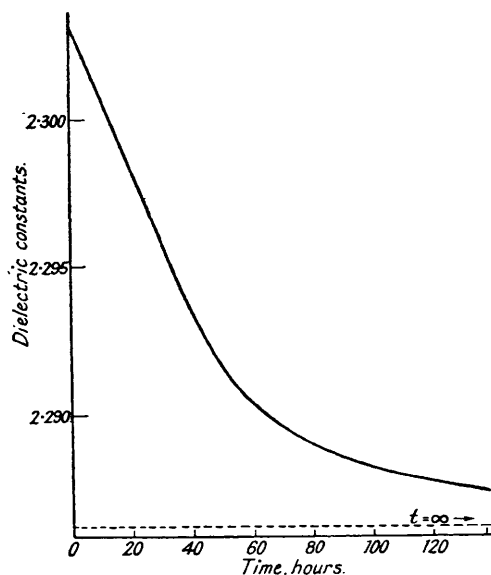
Interconversion of the Diphenyl-4 : 4-bisdiazocyanides in Benzene Solution at 25°.

was bisdiazotised in the cold with sodium nitrite solution (7·8 g. in 125 c.c.), the solution filtered, and treated with aqueous potassium cyanide (containing 8 g.). The bisdiazocyanide separated as an apricot-coloured precipitate, resembling the *p*-halogenobenzenediazocyanides in appearance. It was dissolved in ether (in which it was not very soluble), dried (sodium sulphate), and cooled in carbon dioxide–alcohol, being obtained as a brick-red powder, melting and decomposing suddenly and vigorously at *ca.* 97°. It was fairly stable in air at room temperature, coupled very rapidly with β-naphthol in pure alcoholic solution, and evolved nitrogen when copper-bronze was added to a solution in alcohol.

The more stable form was easily obtained pure by leaving a solution in dry benzene at room temperature for a week, during which a copious deposition of small crystals occurred. These were filtered off, washed with benzene, and air-dried; they formed small maroon-coloured needles, m. p. (explosive decomp.) 208° (after changing colour from 191° onwards), not showing the qualitative reactions mentioned for its isomer, and being notably less soluble in all the common solvents.

		Less stable form.		More stable form.
$100w_1$	0	0·7960	0·7991	0·7960
$\varepsilon_{1200}^{25°}$	2·2725	2·3031	2·3032	(2·2863) *
$d_{40}^{25°}$	0·87378	0·87552	0·87553	(0·8754) *
p_{12} (c.c.)	0·34086	0·34588	0·34590	0·34281
P_1 (c.c.)	—	253	256	151
$n_D^{25°}$	1·49724	—	1·49824	—
r_{12} (c.c.)	0·33503	—	0·33493	—
$[R_L]_D$ (c.c.)	—	—	83·8	—
μ (D.)	—	$2·8_6$	$2·8_9$	$1·8_0$

* Extrapolated from measurements made before crystallisation took place.

The progress of the isomerisation in the case of the solution with $w_1 = 0·00796$ is illustrated in the attached diagram, which shows the change of dielectric constant with time. If the amount of change is assumed proportional to the dielectric-constant change (x), and $\varepsilon = 2·3031$ for time $t = 0$ and $2·2863$ for $t = \infty$, a plot of $\log (0·0168 - x)$ against t is roughly a straight line.

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