**609.** *Some Properties of the Diphenyl-4-diazocyanides and their 4'-Bromo-derivatives.*

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The rates of conversion of the respective labile into the stable forms of diphenyl-4- and 4'-bromodiphenyl-4-diazocyanides have been measured at 25° and 45°. The energies of activation thus obtained agree with forecasts from previous work on the benzenediazocyanides.

The dipole moments of the isomeric diphenyl-4-diazocyanides are found to be 4·5 and 5·5 D. As with the two pairs of naphthalenediazocyanides reported earlier, the stable form has the greater moment, compatible with a *cis–trans*-relationship. Moreover, their ultra-violet absorption spectra in alcoholic solutions are similar but not identical and show the differences expected for geometrical isomers.

THE transformations of various labile diazo-compounds into their stable isomers have been conveniently followed dielectrically or photometrically (Le Fèvre and Vine, *J.*, 1938, 431, 1878; Hartley, *J*, 1938, 633; Le Fèvre and Northcott, *J.*, 1949, 333, 944; Brown, Le Fèvre, and Whittem, *J.*, 1950, 185), and the reactions have been found to be of the first order, with activation energies from 21 to 26 kcals./g.-mol. and frequency factors between $10^{12}$ and $10^{15}$ sec.$^{-1}$.

In particular, Le Fèvre and Northcott (*loc. cit.*) noted that their measurements for a number of benzenediazocyanides conformed to Nathan and Watson's expression (*J.*, 1933, 890, 1248; cf. Watson, *Trans. Faraday Soc.*, 1938, **34**, 165), $E = E_0 \pm C(\mu + \alpha\mu^2)$, where $E$ and $E_0$ are the activation energies for the substituted and unsubstituted compounds respectively, $C$ and $\alpha$ are constants, and $\mu$ is the dipole moment of the corresponding monosubstituted benzene, $C_6H_5X$.

We now record experiments with diphenyl-4-diazocyanide and its 4'-bromo-derivative, undertaken to explore the effect of interpolating an extra aromatic nucleus between the polar C–X link and the inverting $-N{=}N-$ unit. Kinetic observations (by the rate of change of dielectric constant), in benzene as solvent, are summarised in Table I and compared with corresponding data for the benzene derivatives in Table II.

TABLE I.

| Diazocyanide | Diphenyl-4- | 4'-Bromodiphenyl-4- |
|---|---|---|
| $k_{25°}$ from graph, hrs.$^{-1}$ | $0.0629 \pm 0.001$ | $0.105 \pm 0.005$ |
| ,, from $T_{\frac{1}{2}}$, hrs.$^{-1}$ | $0.063$ | $0.100$ |
| $k_{45°}$ from graph, hrs.$^{-1}$ | $0.657 \pm 0.006$ | $1.02 \pm 0.01$ |
| ,, from $T_{\frac{1}{2}}$, hrs.$^{-1}$ | $0.66$ | $1.01$ |
| $E$, kcals./g.-mol. | $22.1_2$ | $21.5_4$ |
| $A$ (from $k_{45°}$), sec.$^{-1}$ | $6.9 \times 10^{11}$ | $1.69 \times 10^{13}$ |
| ,, (from $k_{25°}$), ,, | $7.5 \times 10^{11}$ | $1.71 \times 10^{13}$ |

TABLE II.

| Diazocyanide | $C_6H_5-$ | $C_6H_5 \cdot C_6H_4-$ | $Br \cdot C_6H_5-$ | $Br \cdot C_6H_4 \cdot C_6H_4-$ |
|---|---|---|---|---|
| $k_{25°}$, hr.$^{-1}$ | $5.55$ | $0.063$ | $0.058$ | $0.105$ |
| $k_{45°}$, ,, | — | $0.66$ | — | $1.02$ |
| $E$, kcals./g.-mol. | $23.0$ | $22.1$ | $21.6$ | $21.5$ |
| $A$, sec.$^{-1}$ | $ca. 1 \times 10^{15}$ | $ca. 7 \times 10^{11}$ | $1.5 \times 10^{12}$ | $1.7 \times 10^{13}$ |

*Discussion.*—Of the " direct " and " induced " electrostatic factors which may operate during a reaction, Waters (*J.*, 1933, 1551) has associated the former with the $C\mu$, and the latter with the $C\alpha\mu^2$, term of the Nathan–Watson equation. In a complex inverse manner, therefore, $E$ through a series of compounds should vary with the distances between the polar link and the reaction centre (presumably the azo-group in our cases). Whether $E$ is greater or less than $E_0$ depends mainly upon the sign of $C\mu$ (the magnitude of which is usually greater than $C\alpha\mu^2$).

The moment of a *p*-bromoaryl-group may be regarded as negative. Our findings are therefore in accord with expectations. From Table II it is seen that replacement of hydrogen by bromine leads to a reduction of $E$; further, that in going from $C_6H_5 \cdot C_6H_4 \cdot N_2CN$ to $4'-Br \cdot C_6H_4 \cdot C_6H_4 \cdot N_2CN$ the decrease in $E$ is notably less (about one-half) than that experienced between $C_6H_5 \cdot N_2CN$ and $4-Br \cdot C_6H_4 \cdot N_2CN$.
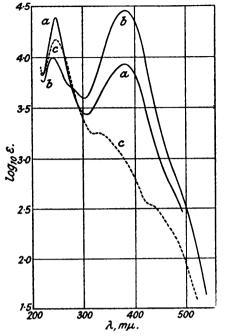
Moreover, the observed $E$ for the bromodiphenyldiazocyanide can be quantitatively brought into line with benzenediazocyanide itself, for which $E_0 = 23.0$ kcals./g.-mol. Le Fèvre and Le Fèvre (*J.*, 1936, 1130) have reported the moment of *p*-bromodiphenyl in benzene as $1.64$ D. Use of this figure in conjunction with the constants derived by Le Fèvre and Northcott (*loc. cit.*, p. 944) yields $E = 21.3$ kcals./g.-mol., comparable with the experimentally found energy, $21.5$ kcals./g.-mol. However, we also find that $E$ for $C_6H_5 \cdot C_6H_4 \cdot N_2CN$ is $22.1$ and not $23.0$ kcals./g.-mol. (forecast from $C_6H_5 \cdot N_2CN$, because $\mu_{\text{Diphenyl}} = 0$). This may indicate no more than that the diphenyl and benzene series of diazocyanides require values of $C$ and $\alpha$ which are not very different from one another. A similar remark may apply to the related naphthalene-$\alpha$- and -$\beta$-compounds, for which $E$ has been recorded as $22.9$ and $23.1$ kcals./g.-mol. (Le Fèvre and Northcott, *loc. cit.*, p. 333).

*The dipole moments of diphenyl-cis- and -trans-4-diazocyanides.* To date, the two naphthalenediazocyanides are the only unsubstituted hydrocarbon-diazocyanides for which the dipole moments of both pairs of isomers have been published.

We now find, by the refractivity method in benzene, that the labile and the stable form of diphenyl-4-diazocyanide have $\mu = 4.5$ and $5.5$ D., respectively. The difference, although smaller, is similar in sense to those previously noted between the forms of the naphthalene compounds :

| | |
|---|---|
| Naphthalene-$\alpha$-diazocyanides | $\delta\mu = 2.4$ D. |
| ,, -$\beta$- ,, | $\delta\mu = 2.9$ D. |
| Diphenyl-4-diazocyanides | $\delta\mu = 1.0$ D. |

In each case the stable isomer is the more polar; this is to be expected if isomeric diazocyanides are configurationally related as *cis-trans*-cyanides (cf. *J.*, 1949, 333, and other references given therein).

*Absorption spectra of the diphenyl-diazocyanides.* These have been determined in alcohol with a Beckman Quartz Photoelectric Spectrophotometer, model DU. Concentrations were $10^{-4}$M. The extinctions near 400 mμ. for the *trans*-variety were re-measured on a $10^{-5}$M-solution.

Results are shown graphically in the figure (curve *a*, *cis*-isomer; curve *b*, *trans*-isomer). The features revealed are those now usually associated with isomers of this type (cf. Le Fèvre and Wilson, *J.*, 1949, 1106, and references cited at the end of *J.*, 1949, 1595).

*Action of light on the isomers.* Indications were obtained, both by dielectric constant and photometric measurements, that daylight caused changes in benzene or alcohol solutions of the type to be expected if a photo-equilibrium were set up between the two forms. Unfortunately, however, decomposition was also accelerated and prevented a clear-cut decision on the point (see Experimental).

### EXPERIMENTAL.

*Preparation of Diazocyanides.*—The methods adopted were essentially those recommended in *J.*, 1938, 431 and 1947, 457, starting materials being obtained as described by Morgan and Walls (*J. Soc. Chem. Ind.*, 1930, **49**, 157), Le Fèvre and Turner (*J.*, 1926, 2045), and Sherwood and Calvin (*J. Amer. Chem. Soc.*, 1946, **64**, 1350).

The extraction of the labile diazocyanides after precipitation at 0° was best accomplished with a mixture of light petroleum (b. p. 40—70°) and ether; even so, emulsions of great persistence were sometimes developed. Refluxing the dried extracts and freezing out the products gave the stable isomers in nearly quantitative yield.

| Diazocyanide. | Colour. | Found, N, %. | Calc., N, %. |
|---|---|---|---|
| Diphenyl-4- (labile) ................................ | Red | 20·0 | 20·2 |
| ,, (stable) ................................ | Dark red | — | — |
| 4'-Bromodiphenyl-4- (labile) .................... | Orange-red | 14·6 | 14·7 |
| ,, (stable) .................... | Red-brown | — | — |

*Rates of Isomerisation.*—The method and apparatus were those recorded in *J.*, 1949, 333. The diazocyanides in benzene appeared extremely susceptible to decomposition, possible causes of which were traces of either moisture or organic impurities (in particular, traces of decomposition products). For this reason, many runs had to be rejected as doubtful or inaccurate. Despite the use of fresh preparations which had been dried at 0° in the dark and allowed to reach room temperature before dissolution, these decompositions could not always be prevented, and in the case of the 4'-nitro-derivative no successful interconversion was completed. Observations were plotted (capacity changes against time) and *k* calculated at successive intervals. The mean *k* so obtained is shown in Table I as " from graph."

*Dipole Moments of the Diphenyldiazocyanides.*—Solutions (prepared in brown bottles) were examined in subdued light as soon as possible after preparation. Procedures, symbols, and apparatus have been described in *J.*, 1949, 333. Measurements are recorded in Table III, in which we include also the values for $P_1$ at each $w_1$, calculated *via* the mixture formula of Sugden (*Trans. Faraday Soc.*, 1934, **30**, 720).

*Action of Light on the Dissolved Diphenyl Isomers.*—Although exposures, for 12 hours, of the above solutions of the labile form at 10 cm. from a 60-watt bulb caused dielectric constant changes such that $αε_2$ became *ca.* 14·9—suggesting a considerable development of the *trans*-isomer—the same treatment of the last-named, dissolved in either benzene or alcohol, induced a slow decomposition with formation of bubbles of gas. In the former solvent the $αε_2$ coefficients of illuminated solutions moved in the direction of that (11·1) ascertained for the labile species but did not reproducibly return to their original values after being kept for 12 hours in the dark.

Parallel photometric experiments at higher dilutions in alcohol showed the effects of decomposition more obviously, *e.g.*, in the figure curve *c* was the absorption curve of a $10^{-4}$M-solution of the *trans*-diazocyanide after 2 hours in sunlight; storage for 24 hours in the absence of light left the spectrum almost unaffected.

TABLE III.

| $100w_1$. | $(\varepsilon_{12})^{25}$. | $(d_{12})_4^{25}$. | $\alpha\varepsilon_2$. | $\beta d_2$. | $P_1$. |
|---|---|---|---|---|---|
| 0 | 2·2725 | 0·87378 | — | — | — |
| *Diphenyl*-4-cis-*diazocyanide* | | | | | |
| 2·9649 | 2·6011 | 0·88086 | 11·08 | 0·239 | 449·5 |
| 4·1965 | 2·7377 | 0·88385 | 11·09 | 0·240 | 436·8 |
| 4·7621 | 2·8043 | 0·88525 | 11·17 | 0·241 | 433·6 |
| *Diphenyl*-4-trans-*diazocyanide* | | | | | |
| 0·2342 | 2·3111 | 0·87423 | 16·48 | 0·192 | 691·1 |
| 1·4430 | 2·5089 | 0·87711 | 16·38 | 0·231 | 655·0 |
| 2·4820 | 2·6785 | 0·87928 | 16·36 | 0·222 | 631·6 |
| 3·8604 | 2·9045 | 0·88201 | 16·37 | 0·213 | 604·4 |

| Isomer. | Mean $\alpha\varepsilon_2$. | Mean $\beta d_2$. | $\infty P_1$. | $[R_L]_D.$* | $\mu$. |
|---|---|---|---|---|---|
| Labile............ | 11·11 | 0·240 | 484·2 c.c. | 65·8 c.c. | 4·5$_2$ D. |
| Stable............ | 16·40 | 0·214 | 692·7 c.c. | 69·7 c.c. | 5·5$_3$ D. |

* Calculated from values already recorded (*J.*, 1938, 431) for the chloro- and bromo-benzene-diazocyanides.