

**139.** *The Orientation of x-Bromo- and x-Nitro-benzocinnoline 6-Oxides.\**

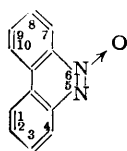
By K. E. CALDERBANK and R. J. W. LE FÈVRE.

The dipole moments of the two compounds named in the title indicate that in both cases the substituent is in the 3-position. Benzocinnolines and their 6-oxides appear to be characterised by ultra-violet absorptions at *ca.* 3000 Å. ( $\log_{10} \epsilon = 3.7-3.9$ ) and 3300—3500 Å. ( $\log_{10} \epsilon = 3.9-4.2$ ), respectively.

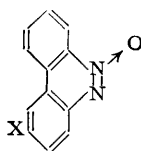
FOLLOWING observations described before (Calderbank and Le Fèvre, *J.*, 1948, 1949) we have examined the products of monobromination and mononitration of benzocinnoline 6-oxide (I).

\* In the paper and in papers discussed therein the Ring Index enumeration for benzocinnoline is used, and the nitrogen carrying the oxygen is numbered 6. Correctly it should be given the lower number possible, *i.e.*, 5.—ED.

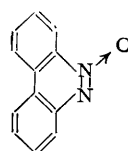
Dielectric-polarisation and spectrographic data for these and related molecules are included in this communication.



(I.)



(II.)



(III.)

*Dipole-moment Measurements.*—In our 1948 paper the moment of benzocinnoline 6-oxide (I) was reported as 5.2 D., while the corresponding datum for benzocinnoline was 3.9 D. Since the link moment of  $N \rightarrow O$  seems to be about 1.7 D. (*i.e.*, the difference between the observed values for *trans*-azo- and -azoxy-benzenes, 0 and 1.7 D., respectively) we may consider the resultant in (I) to be disposed across the molecule in a direction between two and three o'clock and with its negative pole outwards. Provided that the axes 9:10:1:2 and 6:5 are approximately parallel and that no unexpected mesomeric polarisations occur, it is evident that—if  $X = \text{Br}$  or  $\text{NO}_2$ —(II) should be less polar than (III).

On the figures just quoted we calculate the resultant of (I) to lie 75—80° clockwise from the 5 → 6 line. Accordingly, if the vectors associated with bromo- and nitro-group are 1.6 and 4.0, the following moments are to be expected for 2- and 3-monosubstituted derivatives of (I):

|                                   | Substituent at position |            |
|-----------------------------------|-------------------------|------------|
|                                   | (2).                    | (3).       |
| Bromobenzocinnoline 6-oxide ..... | 3.7 D.                  | 5.0—5.2 D. |
| Nitrobenzocinnoline 6-oxide ..... | 1.7—1.0                 | 5.7—6.0    |

From measurements tabulated later polarities are actually found as follow:

|   |        |
|---|--------|
| 3:8-Dichlorobenzocinnoline 6-oxide .....    | 5.1 D. |
| <i>α</i> -Bromobenzocinnoline 6-oxide ..... | 5.3    |
| <i>α</i> -Nitrobenzocinnoline 6-oxide ..... | 5.6    |

The disubstituted oxide is included to test the assumption of colinearity of the "diphenyl" part of (I); if this is correct the moment of the 3:8-dichloro-compound should be very close to that (5.2 D.) of its parent. Agreement is, in fact, highly satisfactory.

On the argument used above, the mono-bromo- and -nitro-derivatives appear to be 3-isomers in each case. Such an inference is contrary to King and King's conclusions (*J.*, 1945, 824) where nitration is concerned. These authors found benzocinnoline 6-oxide to give, with fuming nitric acid, mainly that nitro-product, m. p. 269°, to which our measurements relate, together with smaller amounts of an isomer, m. p. 226°. By total reduction, followed by ring-closure, etc., aminocarbazoles, m. p. 243° and 240°, were isolated, recognised by their melting points as 3-aminocarbazole (Ullmann, *Annalen*, 1903, 332, 101), and 2-aminocarbazole (Blank, *Ber.*, 1891, 24, 306), respectively. Yet the m. p.s quoted in the literature (*cf.* Beilstein, "Handbuch," Vol. XXII, p. 460) are 238° for the 2-derivative, and 246—248°, or 254°, or 240—259° (decomp.) for the 3-derivative. It does not appear from King and King's paper that they determined mixed m. p.s or directly compared authentic specimens of the aminocarbazoles with their own end products. We suggest therefore that the orientations of the nitro-compounds, m. p. 269° and 226°, have not yet been rigidly demonstrated by chemical methods.\*

*Absorption Spectra.*—These have been determined in *m*/20,000-ethyl alcoholic solution with the Beckman Photoelectric Quartz Spectrophotometer, Model D.U. The wave-lengths and extinctions ascribable to general conjugation between the  $-N=N-$  systems and the associated

\* The point has been discussed with Professor F. E. King and Dr. T. J. King who comment as follows. "The identification of the aminocarbazole derived from the principle nitration product, m. p. 269°, of benzocinnoline 6-oxide was based on the correspondence of the m. p. (218°) of its analytically pure *N*-acetyl compound and that of 3-acetamidocarbazole (217°) as determined by Ullmann (*loc. cit.*). Owing to the lack of concordance between the literature values for 3-aminocarbazole, less importance can be attached to the decomposition temperature (240°; 243°, after crystallisation) of the corresponding aminocarbazole (King and King, *loc. cit.*, where Ullmann's m. p. for 3-aminocarbazole is inexplicably misquoted), although it is higher than that of 2-aminocarbazole (238°). Nevertheless, in view of the dipole determination by Calderbank and Le Fèvre, our conclusions as to the orientation of the nitro-cinnoline 6-oxides cannot be maintained."

Ar-nuclei [*K* bands on Braude's classification (*Ann. Reports*, 1945, **42**, 105), cf. Cook, Jones, and Polya, *J.*, 1939, 1315] are listed in the following table :

|                           | $\lambda_{\max.}$ | $\log_{10} \epsilon.$ |                            | $\lambda_{\max.}$ | $\log_{10} \epsilon.$ |
|---------------------------|-------------------|-----------------------|----------------------------|-------------------|-----------------------|
| Benzocinnoline .....      | 3000              | 3.87                  | Benzocinnoline oxide ..... | 3320              | 3.97                  |
| 1 : 10-Dimethyl- ,, ..... | 2940              | 3.73                  | 3 : 8-Dichloro- ,, .....   | 3320              | 3.86                  |
| 3 : 8-Dichloro- ,, .....  | 3060              | 3.74                  | <i>x</i> -Nitro- ,, .....  | 3420              | 4.12                  |
|                           |                   |                       | <i>x</i> -Bromo- ,, .....  | 3440              | 4.01                  |

The seven examples fall into two groups, the oxides absorbing at wave-lengths *ca.* 300  $\mu$ . longer than the benzocinnolines, and with a slightly greater intensity. *cis*-Azo- and -azoxy-benzenes [ $\lambda_{\max.}$  ( $\log_{10} \epsilon$ ) : 3050 (3.5) and 3350 (3.9), respectively] also fit this generalisation. The points made by Calderbank and Le Fèvre (*J.*, 1948, 1949) therefore receive further support.

#### EXPERIMENTAL.

Benzocinnoline 6-oxide (m. p. 138°) and its mononitration product (m. p. 269°) were prepared as described by King and King (*loc. cit.*). 1 : 10-Dimethyl- and *x*-bromo-benzocinnoline 6-oxides were presented to us by Mr. P. H. Gore, M.Sc. (who will be describing the latter in a separate publication; the former, m. p. 153°, was first isolated by Sako, see below). The 3 : 8-dichloro-oxide was obtained by reducing 4 : 4'-dichloro-2 : 2'-dinitrodiphenyl (Ullmann and Bielecki, *Ber.*, 1901, **34**, 2176) by Sako's sodium sulphide nonahydrate method (*Bull. Chem. Soc. Japan*, 1934, **9**, 393); after recrystallisation from benzene and then alcohol it formed pale-yellow needles, m. p. 244—245° (Found : C, 54.1; H, 2.35; N, 10.5; Cl, 26.8.  $C_{12}H_8ON_2Cl_2$  requires C, 54.4; H, 2.3; N, 10.6; Cl, 26.75%). Nitration by dissolution in absolute nitric acid on the water-bath followed by pouring on ice, etc., gave a cream-coloured powder, crystallisable from acetic acid, but sparingly soluble in other solvents. Analysis suggested that it was a dinitro-derivative, m. p. 294—295° (Found : N, 15.6.  $C_{12}H_8O_5N_4Cl_2$  requires N, 15.8%). "Sako" reductions of 3 : 3' : 5 : 5'-tetrachloro- and 3 : 3' : 4 : 4' : 5 : 5'-hexachloro-2 : 2'-dinitrodiphenyls (Roosmalen, *Rec. Trav. chim.*, 1934, **53**, 359) yielded products with high m. p.s and little solubility in organic solvents.

3 : 8-Dichloro- and 1 : 10-dimethyl-benzocinnolines were obtained by reducing the corresponding oxides with the calculated quantities of stannous chloride in concentrated hydrochloric acid. They formed small, pale-yellow (m. p. 259—260°) and colourless (m. p. 135—136°) crystals from alcohol (Found : N, 11.15 and 13.3 respectively.  $C_{12}H_8N_2Cl_2$  requires N, 11.25.  $C_{14}H_{12}N_2$  requires N, 13.4%).

The measurements tabulated below were made at 25°, benzene being used as solvent. Symbols and procedures for calculation have been explained previously (Calderbank and Le Fèvre, *loc. cit.*, cf. also Le Fèvre, *Trans. Faraday Soc.*, 1950, **46**, 1).

| Measurements.  |                         |              |                 |               |             |                         |              |                 |               |
|--|-------------------------|--------------|-----------------|---------------|-------------|-------------------------|--------------|-----------------|---------------|
| 100 $w_1$ .  | $\epsilon_{25^\circ}$ . | $d_4^{25}$ . | $a\epsilon_2$ . | $\beta d_2$ . | 100 $w_1$ . | $\epsilon_{25^\circ}$ . | $d_4^{25}$ . | $a\epsilon_2$ . | $\beta d_2$ . |
| 0  | 2.2725                  | 0.87378      | —               | —             | —           | —                       | —            | —               | —             |
| 3 : 8-Dichlorobenzocinnoline 6-oxide.  |                         |              |                 |               |             |                         |              |                 |               |
| 0.2017   | 2.2931                  | 0.87450      | 10.21           | 0.357         | 0.4112      | 2.3125                  | 0.87529      | 9.73            | 0.367         |
| 0.2613   | 2.3004                  | 0.87470      | 10.68           | 0.352         | 0.5321      | 2.3225                  | —            | 9.40            | —             |
| 0.2971   | 2.3016                  | 0.87486      | 9.80            | 0.363         |             |                         |              |                 |               |
| Whence ( $a\epsilon_2$ ) $w_1 = 10.99-301w_1$ ; $\Sigma(d_{12} - d_2)/\Sigma w_1 = 0.3611$ . |                         |              |                 |               |             |                         |              |                 |               |
| Nitrobenzocinnoline 6-oxide (m. p. 269°).  |                         |              |                 |               |             |                         |              |                 |               |
| 0.1854   | 2.2979                  | 0.87451      | 13.70           | 0.394         | 0.2645      | 0.3064                  | 0.87494      | 12.74           | 0.439         |
| 0.2112   | 2.3000                  | 0.87470      | 13.00           | 0.436         | 0.3012      | 2.3105                  | 0.87492      | 12.62           | 0.379         |
| Whence ( $a\epsilon_2$ ) $w_1 = 15.02-837w_1$ ; $\Sigma(d_{12} - d_2)/\Sigma w_1 = 0.4105$ . |                         |              |                 |               |             |                         |              |                 |               |
| Bromobenzocinnoline 6-oxide (m. p. 194.5°).  |                         |              |                 |               |             |                         |              |                 |               |
| 0.0695   | 2.2806                  | 0.87396      | 11.65           | 0.259         | 0.2024      | 2.2952                  | 0.87477      | 11.21           | 0.489         |
| 0.1595   | 2.2908                  | 0.87437      | 11.47           | 0.370         | 0.3181      | 2.3085                  | 0.87501      | 11.32           | 0.387         |
| Whence ( $a\epsilon_2$ ) $w_1 = 11.67-140w_1$ ; $\Sigma(d_{12} - d_2)/\Sigma w_1 = 0.3989$ . |                         |              |                 |               |             |                         |              |                 |               |

#### Calculation of results.

| Benzocinnoline 6-oxide. | $M_1$ . | ( $a\epsilon_2$ ) $w_1=0$ . | Mean $\beta$ .     | $\infty P_1$ . | $[R_L]_D^*$ | $\mu, D$ .       |
|-------------------------|---------|-----------------------------|--------------------|----------------|-------------|------------------|
| 3 : 8-Dichloro- .....   | 265.0   | 10.9 <sub>9</sub>           | 0.413 <sub>3</sub> | 600.8          | 75.9        | 5.0 <sub>8</sub> |
| <i>x</i> -Nitro- .....  | 241.1   | 15.0 <sub>2</sub>           | 0.469 <sub>8</sub> | 724.7          | 72.5        | 5.6 <sub>4</sub> |
| <i>x</i> -Bromo- .....  | 275.0   | 11.6 <sub>7</sub>           | 0.456 <sub>5</sub> | 654.6          | 74.0        | 5.3 <sub>2</sub> |

\* Taking  $R_H = 1.10$ ,  $R_{Cl} = 5.97$ ,  $R_{NO_2} = 7.36$ ,  $R_{Br} = 8.86$  in conjunction with the previously observed value of 66.2 c.c. for the unsubstituted oxide (Calderbank and Le Fèvre, *loc. cit.*)

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