

oxide has been measured at 650 mm. and at various temperatures.

2. Copper, when dispersed in calcium oxide, is a better adsorbent for hydrogen than is the pure copper.

3. In general the activated adsorption of hydrogen on calcium oxide and on copper dispersed

in calcium oxide resembles the adsorption of hydrogen on magnesia and on copper dispersed in magnesia.

4. An equation has been suggested, the use of which permits the more uniform treatment of the data for copper dispersed in oxides.

SALT LAKE CITY, UTAH

RECEIVED AUGUST 21, 1939

## NOTES

### Note on the Dipole Moment of 1-Chloroanthraquinone

BY ERNST BERGMANN AND ANNA WEIZMANN

In connection with a stereochemical investigation in the series of anthracene dichlorides, we

to calculate the electric moment, instead of extrapolating to infinite dilution, which would have given even a slightly higher figure.

The *significance* of figures in the tables is as in previous communications.

$\tau$	$\rho$	$\epsilon$	$n^2$	$P^{1/2}$	$P_E^{1/2}$	$P$	$P_E$	$P_{A+O}$
Dioxane solution; $t = 24.2^\circ$								
0	1.0276	2.2553	2.0135	25.2628	21.6250	....	...	...
0.00906	1.0350	2.3200	2.0278	26.3919	22.0405	149.91	67.51	82.40
.01566	1.0404	2.3562	2.0392	27.0544	22.3584	139.62	68.43	71.19
.01739	1.0418	2.3645	2.0415	27.2100	22.4300	137.23	67.90	69.31
$P_{A+O}^\infty = 74.30; \mu = 1.9 D$								
Benzene solution: $t = 24.6^\circ$								
0	0.8732	2.2747	2.2404	26.6302	26.1288	....	...	...
0.00914	.8832	2.3220	2.2506	27.5327	26.4831	124.69	64.88	59.81
.01282	.8872	2.3468	2.2570	27.9744	26.6447	131.06	66.39	64.67
.01817	.8930	2.3923	2.2627	28.7420	26.8606	142.53	66.40	76.13
$P_{A+O}^\infty = 66.87; \mu = 1.8 D$								

reported, a short time ago,<sup>1</sup> some figures on the dipole moment of chloroanthraquinone, which we calculated to 1.9 *D*. Fischer and Rogowski<sup>2</sup> arrived recently at lower figures of 1.53 (in benzene) and 1.55 (in dioxane), respectively. Although without influence on the general results put forward in our paper, we have reinvestigated 1-chloroanthraquinone both in benzene and again in dioxane solution and have found 1.8 and 1.9 *D*, respectively. Following the procedure of the German authors, we have taken the average of the (atomic and) orientation polarization in order

(1) E. Bergmann and A. Weizmann, *THIS JOURNAL*, **60**, 1801 (1938).

(2) Fischer and Rogowski, *Physik. Z.*, **40**, 331 (1939).

THE DANIEL SIEFF RESEARCH INSTITUTE  
REHOVOTH, PALESTINE

RECEIVED JULY 5, 1939

### The Optical Activity of $\alpha$ -Bromopropionitrile

BY KENNETH L. BERRY AND JULIAN M. STURTEVANT

In connection with recent physical theories of optical rotatory power,<sup>1,2</sup> it would be of interest to know the optical properties of one or more compounds of simple, fixed structure, *i. e.*, compounds containing one asymmetric carbon atom substituted by four groups having optical axes of symmetry parallel with the valence bonds to the asymmetric carbon atom.

(1) Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937).

(2) Condon, Altar and Eyring, *ibid.*, **5**, 753 (1937).

The simplest molecule heretofore available for purposes of comparison of theory with experiment is secondary butyl alcohol.<sup>1,3,4</sup> In view of the uncertainties introduced by the non-linearity of the ethyl and hydroxyl groups, this substance has proved not too satisfactory. Therefore,  $\alpha$ -bromopropionitrile has been prepared in an optically active form, since it appears reasonable to assume that each of the groups attached to the asymmetric carbon atom has cylindrical symmetry. Strong evidence in favor of this assumption in the case of the nitrile group is given by Brockway,<sup>5</sup> who demonstrated the linearity of C—C≡N in methyl cyanide by the electron diffraction method, and by Weissberger and Sängewald,<sup>6</sup> who found a zero dipole moment for *p*-dicyanobenzene. The result of Bretscher<sup>7</sup> attributing a relatively large moment to 4,4'-dicyanodiphenyl has been considered anomalous by Le Fèvre and Vine,<sup>8</sup> and as not proving any lack of axial symmetry in this molecule.

Kirkwood's theory leads to the following simple expression for the rotatory parameter of an active molecule in terms of the geometrical configuration and the polarizability tensors of its constituent groups

$$g = g^{(0)} + g^{(1)} + \sum_{k=1}^{N+1} g_k$$

In molecules with only one asymmetric center the  $g_k$  vanish. Each term in  $g^{(0)}$  vanishes if the optical axes of symmetry of the groups are parallel to the respective bonds linking them to the asymmetric carbon atom. The rotatory power must then be sought in higher terms which are considered by Kirkwood to be relatively unimportant. Thus  $\alpha$ -bromopropionitrile might be expected to have a small specific rotation.

*l*- $\alpha$ -Bromopropionitrile was prepared from *l*- $\alpha$ -bromopropionic acid by asymmetric conversion. The rotation of the acid indicated it to be 67.1% levo and 32.9% dextro. It was converted to the amide and the latter dehydrated with phosphorus pentoxide to obtain the nitrile. After one distillation the nitrile had a specific rotation  $[\alpha]^{25}_D -5.29^\circ$ , and after a second distillation  $[\alpha]^{25}_D -5.25^\circ$ . The final product analyzed 10.44, 10.50, and 10.49% nitrogen (calcd. for CH<sub>3</sub>CHBrCN,

10.46%). On the assumption that no racemization occurred during the synthesis, the calculated specific rotation for the optically pure compound is  $[\alpha]^{25}_D -15.33^\circ$ . The true value would, of course, be higher if some racemization had occurred.

On first sight, this result indicates that greater importance should be attached to the higher approximations of the polarizability theory. Kirkwood<sup>9</sup> points out, however, that it is not unquestionable evidence since lateral optical anisotropy of sufficient magnitude to account for the observed rotation could be induced in the CN group, probably by the C-Br dipole.

Since this molecule is of considerable interest from a theoretical point of view, efforts will be made to prepare it in a state of higher optical purity. The refractive and rotatory dispersion behavior of the substance in the visible region will be determined.

A more unambiguous test of the importance of the higher terms in Kirkwood's theory would presumably be furnished by a molecule having only monatomic groups attached to the asymmetric carbon atom. Because of this fact and its general theoretical interest, fluorochlorobromomethane, CHFCIBr, has been prepared. Attempts are at present being made to resolve it by various methods.

(9) Kirkwood, private communication.

STERLING CHEMISTRY LABORATORY  
YALE UNIVERSITY  
NEW HAVEN, CONN.

RECEIVED OCTOBER 20, 1939

## Desoxycholamine

BY WILLIAM T. CALDWELL

In an article describing the preparation of cholamine by Lindemann's modification of the Curtius reaction,<sup>1</sup> attention was called to the fact that Borsche and Schwarz had distilled with caustic potash the urethan derived from cholylazide without, however, obtaining any of the desired amine by this application of the usual Curtius degradation. It was very interesting, therefore, to receive from Dr. Mihail Vanghelovici, in a private communication which he kindly sent, a description of a desoxycholamine whose preparation he reported to the Rumanian Academy of Sciences. He observed that, since his desoxycholamine had been prepared by the Curtius method, working at a pressure of 2 mm., it appeared to be

(1) Caldwell, THIS JOURNAL, 60, 991 (1938).

(3) Gorin, Walter and Eyring, *J. Chem. Phys.*, 6, 824 (1938).

(4) Kuhn, *Z. physik. Chem.*, 331, 23 (1936).

(5) Brockway, THIS JOURNAL, 58, 2516 (1936).

(6) Weissberger and Sängewald, *J. Chem. Soc.*, 855 (1935).

(7) Bretscher, *Helv. Phys. Acta*, 2, 257 (1929).

(8) Le Fèvre and Vine, *J. Chem. Soc.*, 1878 (1938).