

TABLE I

QUANTUM YIELDS AND RELATIVE RATE CONSTANTS OF DPPH  
PHOTOREDUCTION IN VARIOUS SOLVENTS

Solvent	$k$ (e.p.r.), min. <sup>-1</sup>	$k$ (col.), min. <sup>-1</sup>	$\phi^a$	$\phi^b$	$k_2/k_3$
Benzene					
Cumene	0.198	0.212	1.3	1.2	0.66
Toluene	.0538	...	0.53	0.48	3.16
Hexane	.0388	0.0411	.38	.35	4.71
Cyclohexane	.0608	0.0648	.57	.54	2.70
Methylcyclohexane	.0823	...	.75	.72	1.77

<sup>a</sup> Determined using disappearance of Ph<sub>2</sub>CO in IPA as an actinometer. <sup>b</sup> Determined using formation of acetone in Ph<sub>2</sub>CO-IPA photolysis as an actinometer.

photometer with the exciting light (>3100 Å.) at an angle to the pellet. In the absence of light no reaction was observed; however, during irradiation the pellet gradually turned from purple to yellow and the infrared spectrum changed from that of the DPPH to one identical with DPPH<sub>2</sub>. Further studies of this effect are being conducted and we are now extending this technique to some quantitative studies of photochemical reactions in the solid state.

**Acknowledgment.**—This research was supported in part by grants from the Division of Air Pollution, Bureau of State Services, Public Health Service, Grant AP 00109, and an Air Force Contract, AF 19(604)-8096, from the Geophysics Research Directorate of the Air Force Cambridge Research.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF CALIFORNIA  
RIVERSIDE, CALIFORNIA

J. N. PITTS, JR.  
E. A. SCHUCK  
J. K. S. WAN

RECEIVED NOVEMBER 22, 1963

### Circular Dichroism and Rotatory Dispersion Curves for Helices<sup>1</sup>

Sir:

The excited state of a polymeric array can be considered an exciton band of many, closely spaced energy levels. A transition to one of these levels can have a large rotational strength and a small oscillator strength or *vice versa*, therefore a simple proportionality between the entire absorption band and the circular dichroism curve is not necessarily expected. For a helix the component of the absorption band polarized perpendicular to the helix axis gives rise to a unique circular dichroism curve as shown in Fig. 1. Qualitatively, the shape of the circular dichroism curve arises from many rotational strengths occurring near  $\lambda_0$ , the wave length of maximum absorption of the perpendicular band. The rotational strengths are all positive on one side of  $\lambda_0$  and negative on the other. They decrease in magnitude as  $|\lambda - \lambda_0|$  increases and the sum of all rotational strengths is zero. This leads to canceling of the circular dichroism at  $\lambda_0$  and nearly equal and opposite curves on either side as seen in Fig. 1. The rotational strengths responsible for this circular dichroism curve were ignored in Moffitt's<sup>2</sup> classical paper. As his original approximation led to only one transition at  $\lambda_0$  (instead of many near  $\lambda_0$ ), the one rotational strength (equivalent to the sum of present rotational strengths) was equal to zero. Moffitt, Fitts, and Kirkwood<sup>3</sup> corrected the mistake, but did not discuss circular dichroism or optical rotatory dispersion near an absorption band. Mason's<sup>4</sup>

(1) Supported in part by research grant GM-10840 from the Institute of General Medical Sciences Public Health Service, by an unrestricted grant from Research Corporation, and by the U. S. Atomic Energy Commission.

(2) W. Moffitt, *J. Chem. Phys.*, **25**, 467 (1956).

(3) W. Moffitt, D. D. Fitts, and J. G. Kirkwood, *Proc. Natl. Acad. Sci. U. S. A.*, **43**, 723 (1957).

(4) S. F. Mason, *Quart. Rev. (London)*, **17**, 20 (1963).

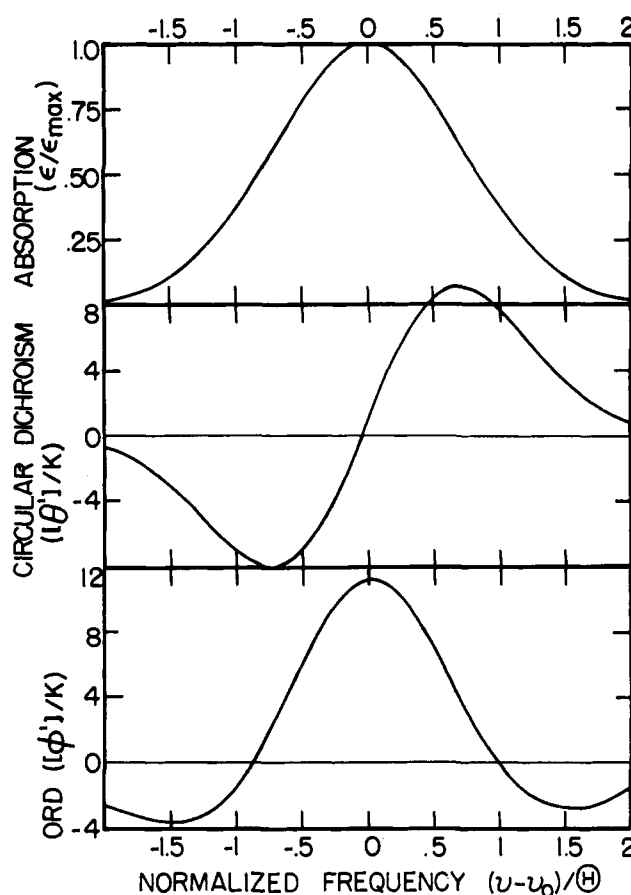


Fig. 1.—The absorption, circular dichroism, and optical rotatory dispersion for a perpendicularly polarized band in a helix. The absorption is assumed to be gaussian in frequency (ref. 5) and  $K$  is defined in ref. 6.

recent claim that this correction is unimportant is wrong.

The circular dichroism curve seems broader than the absorption curve, because its maximum and minimum occur where the absorption has fallen to about 60% of its maximum value.<sup>5</sup> The sign of the circular dichroism curve is determined by  $\sum_{j>i}^N (j-i)V_{ij} \sin 2\pi j/P$ , where  $V_{ij}$  is the potential of interaction of groups  $i$  and  $j$  and  $P$  is the number of groups per turn.<sup>6</sup> The predicted rotatory dispersion (ORD) curve can be obtained from the Kronig-Kramers relation<sup>9</sup> and is also given in Fig. 1.

These curves provide a different interpretation for the recently published circular dichroism data on polynucleotides.<sup>10</sup> For poly A, Brahms finds (ref.

(5) For an absorption curve gaussian in frequency, the maximum and minimum in the circular dichroism curve appear approximately at  $\nu - \nu_0 = \pm\Theta/\sqrt{2}$ , therefore this corresponds to  $\epsilon = \epsilon_{\max} \exp[-(\nu - \nu_0)^2/\Theta^2] = \epsilon_{\max} \exp(-1/2)$ .

(6) The equation for the circular dichroism curve for a single strand helix corresponding to a gaussian absorption curve polarized perpendicular to the helix axis is

$$[\theta'] = K[2(\nu - \nu_0)\nu_0/\Theta^2 + 1] \exp[-(\nu - \nu_0)^2/\Theta^2]$$

$$K = (48\pi^{3/2}N_0z\nu_0\mu_{\perp}^2/h^2c^2\Theta) \left[ \sum_{j>i}^N (j-i)V_{ij} \sin 2\pi j/P \right]$$

where  $z$  is the pitch of the helix and  $\mu_{\perp}$  is the electric transition moment. It can be derived from an expression for rotational strength for light incident parallel to the helix axis. A very similar expression holds for a double stranded helix.<sup>7</sup>

(7) I. Tinoco, Jr., R. W. Woody, and D. F. Bradley, *J. Chem. Phys.*, **38**, 1317 (1963).<sup>8</sup>

(8) See eq. A12 and A14 for the single strand helix and eq. A20 and A21 for the double strand helix.

(9) A. Moscowitz, *Advan. Chem. Phys.*, **4**, 67 (1962).

(10) J. Brahms, *J. Am. Chem. Soc.*, **85**, 3298 (1963).

10, Fig. 2) that the circular dichroism is zero near the absorption maximum at 252 m $\mu$  and has a maximum and minimum at wave lengths where the absorption is about 60% of its maximum. The circular dichroism curve is not symmetric as predicted for an isolated absorption band, but the spectrum shows an overlapping of the 200 m $\mu$  band. We therefore propose that the measured circular dichroism is caused by a perpendicularly polarized absorption band in poly A centered at 250 m $\mu$ . It follows that the positive lobe of this circular dichroism curve is not primarily caused by an  $n \rightarrow \pi^*$  transition at 262 m $\mu$ . A calculation of the sign of the circular dichroism curve for poly A<sup>11</sup> gives results in agreement with experiment and thus further supports our interpretation.

The poly U data are analogous to poly A and presumably have the same explanation. The poly C circular dichroism curve shows a single peak, but as the poly C spectrum is more complicated and the poly C geometry is not known, no interpretation can be given at this time.

DNA should show the behavior given in Fig. 1. The circular dichroism maximum and minimum<sup>12</sup> and ORD trough and two peaks<sup>13</sup> are in good agreement with those calculated from the DNA spectrum.

Polypeptide helices also show the type of circular dichroism and ORD curves given in Fig. 1. However, these helices have the complication of normal circular dichroism curves also being present in the same wave length region. The amide transition moments are tilted with respect to the helix axis instead of being essentially either parallel or perpendicular to it as in DNA-like helices. This leads to normal circular dichroism curves at the absorption maxima of the parallel and perpendicular components of the tilted transition moments. Furthermore, there is apparently a contribution from the amide carbonyl  $n \rightarrow \pi^*$  transition.<sup>14,15</sup> Calculation of the sum of these effects leads to satisfactory agreement with experiment.<sup>16</sup>

In summary all single or multistranded helices with an absorption band polarized perpendicular to the helix axis should show the effect given in Fig. 1. However, the effect can be easily resolved only for an isolated band. Therefore, helical dye arrays would seem to provide the best example. One can also orient the helices and measure the rotation or circular dichroism for light incident parallel to the helix axis; only perpendicularly polarized transitions will contribute.

**Acknowledgment.**—We wish to thank Prof. J. T. Yang, San Francisco Medical Center, for helpful suggestions.

(11) The parameters necessary for this calculation are given in ref. 8. The ORD curves for oligomers of adenylic acid containing up to 10 base pairs are shown in ref. 7, Fig. 3.

(12) J. Foss, Iowa State University, unpublished.

(13) J. T. Yang and T. Samejima, *J. Am. Chem. Soc.*, **85**, 4039 (1963).

(14) J. A. Schellmann and P. Oriol, *J. Chem. Phys.*, **37**, 2114 (1962).

(15) R. W. Woody, Ph.D. Thesis, University of California, Berkeley, 1963.

(16) R. W. Woody and I. Tinoco, Jr., unpublished.

CHEMISTRY DEPARTMENT  
UNIVERSITY OF CALIFORNIA  
BERKELEY 4, CALIFORNIA

IGNACIO TINOCO, JR.

RECEIVED NOVEMBER 7, 1963

## The Selective Oxidation of Arylcarbinols to Aldehydes<sup>1</sup> Sir:

Recently, Pfitzner and Moffatt<sup>2</sup> have reported that the oxidation of alcohols in the presence of phosphoric

(1) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this research.

(2) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963).

acid, dicyclohexylcarbodiimide, and dimethyl sulfoxide produced aldehydes and ketones. This reaction appears to involve dimethyl sulfoxide as a reactant and resembles an earlier report by Kornblum<sup>3</sup> and Nace and Monagle,<sup>4</sup> who obtained aldehydes from the reaction of primary halides or tosylates with dimethyl sulfoxide.

In continuation of our study of the reactions of alcohols in dimethyl sulfoxide,<sup>5</sup> we wish to report the selective oxidation of a variety of benzyl alcohols to the corresponding aldehydes. This oxidation proceeded conveniently by refluxing the alcohol in dimethyl sulfoxide and was facilitated by passing a stream of air through the reaction medium. The reaction stopped at the aldehyde stage with over-oxidation to the acid occurring in only one case in 3% yield. In fact, when a solution of benzaldehyde in dimethyl sulfoxide was refluxed (190°) for 24 hr. with air passing through the solution, only 1.6% benzoic acid was isolated with 87% benzaldehyde recovered. The unique feature of these observations is the role of dimethyl sulfoxide in inhibiting further oxidation of aldehydes yet permitting the oxidation of alcohols.

The following procedure is representative of this oxidation. A solution of benzyl alcohol (10.8 g., 0.10 mole) and dimethyl sulfoxide (54.6 g., 0.70 mole) was heated for 14 hr. at reflux with air passing through the solution. The mixture was cooled, diluted with water, extracted with ether, and the ether extract washed with water, dried, and distilled. The yield of pure benzaldehyde, b.p. 75–77° (22 mm.),  $n_D^{20}$  1.5440, 2,4-dinitrophenylhydrazone m.p. 236–237°, was 8.5 g. (80%). Table I contains a variety of examples which were subjected to these conditions for 4 to 48 hr. Unless stated otherwise, the yields in Table I represent isolated purified material.

TABLE I  
OXIDATION OF BENZYL ALCOHOLS TO ALDEHYDES

Alcohol	Product	% yield
<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> CHO	77 <sup>a</sup>
<i>m</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	<i>m</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> CHO	63 <sup>b</sup>
<i>o</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	<i>o</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> CHO	27 <sup>c</sup>
<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> CHO	86
<i>o</i> -Cl-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	<i>o</i> -Cl-C <sub>6</sub> H <sub>4</sub> CHO	78
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	C <sub>6</sub> H <sub>5</sub> CHO	80
<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> CHO	85
<i>p</i> -CH <sub>3</sub> -O-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	<i>p</i> -CH <sub>3</sub> -O-C <sub>6</sub> H <sub>4</sub> CHO	8.8
C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> OH	( <i>p</i> -CH <sub>3</sub> -O-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ) <sub>2</sub> -O	85
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	C <sub>6</sub> H <sub>5</sub> CH=CHCHO	60 <sup>d</sup>
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	26
	O	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHOHCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CCH <sub>3</sub>	25 <sup>d</sup>
	C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>3</sub>	36 <sup>d</sup>

<sup>a</sup> Crude yield of 90%. <sup>b</sup> An additional 13.5% of the aldehyde was isolated as the 2,4-dinitrophenylhydrazone. <sup>c</sup> This was isolated as the 2,4-dinitrophenylhydrazone. <sup>d</sup> These yields were determined by vapor phase chromatography.

Although air facilitates the reaction, oxygen does not appear to be the oxidant. There was no oxygen uptake when the oxidation of benzyl alcohol was performed over a measured volume of oxygen under conditions which produced benzaldehyde in 60% yield. In this experiment dimethyl sulfide, identified by the mercuric chloride derivative, m.p. 146–148° (lit.<sup>6</sup> m.p. 150–151°),

(3) N. Kornblum, W. J. Jones, and G. J. Anderson, *ibid.*, **81**, 4113 (1959).

(4) H. R. Nace and J. J. Monagle, *J. Org. Chem.*, **24**, 1792 (1959).

(5) V. J. Traynelis, W. L. Hergenrother, J. R., Livingston, and J. A. Valicenti, *ibid.*, **27**, 2377 (1962); V. J. Traynelis, W. L. Hergenrother, and in part H. T. Hanson and J. A. Valicenti, *ibid.*, **29**, 123 (1964).

(6) W. F. Faragher, J. C. Morrell, and S. Comay, *J. Am. Chem. Soc.*, **51**, 2781 (1929).