TABLE IV

| hkl | F, exptl. | F, calcd. C–C = 1.48 | F, calcd. C–C = 1.41 |
|---|---|---|---|
| 008 | 49.5 | 49.3 | 37.4 |
| 009 | 53.0 | 53.1 | 65.0 |
| $20\bar{7}$ | 40.5 | 38.1 | 27.3 |
| $20\bar{8}$ | 63.6 | 66.0 | 75.3 |

Probable positions for the 48 carbon atoms in the unit cell are $x,y,z$; $\bar{x},\bar{y},\bar{z}$; $^1/_2 + x$, $^1/_2 - y,z$; $^1/_2 - x$, $^1/_2 + y,\bar{z}$; the values of $x,y,z$ for the twelve carbon atoms in the half molecule are as follows

| Atom | x | y | z |
|---|---|---|---|
| 1 | −0.018 | 0 | 0.040 |
| 2 | + .043 | +0.186 | .089 |
| 3 | + .009 | + .186 | .165 |
| 4 | − .087 | 0 | .192 |
| 5 | − .149 | − .186 | .144 |
| 6 | − .115 | − .186 | .067 |
| 7 | − .123 | 0 | .272 |
| 8 | − .061 | + .186 | .321 |
| 9 | − .096 | + .186 | .398 |
| 10 | − .192 | 0 | .425 |
| 11 | − .254 | − .186 | .376 |
| 12 | − .220 | − .186 | .300 |

The writer wishes to acknowledge with appreciation the grant of the European Fellowship from the American Association of University Women which made possible the work; and to express to Sir William Bragg and the Managers of the Royal Institution her thanks for the privilege of making the measurements in the Davy Faraday Laboratory, and to Dr. K. Lonsdale for her helpful interest in the work.

## Summary

Additional experimental data concerning the crystal structures of five biphenyl derivatives are presented.

The unit cell of quaterphenyl has the dimensions $a$ = 8.05 Å., $b$ = 5.55 Å., $c$ = 17.81 Å., $\beta$ = approximately 95.8° and contains two centrosymmetrical molecules. Trial and error analyses together with a one-dimensional Fourier projection indicate that the molecules are oriented at an angle of 17.3° to the normal to the (001) plane in the acute angle $\beta$ and that the carbon–carbon distance between benzene rings is 1.48 Å.

SOUTH HADLEY, MASS. RECEIVED AUGUST 3, 1936

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WELLESLEY COLLEGE]

# Ultraviolet Absorption and Rotatory Dispersion of 3-Methylcyclohexanone[1]

BY H. S. FRENCH AND M. NAPS

The rotatory dispersion within an absorption band has thus far been recorded for only a limited number of compounds. We have been especially interested in such work on compounds containing the carbonyl group. It has been proved conclusively for several of these carbonyl compounds, especially camphor,[2] camphor-$\beta$-sulfonic acid,[3] and carvomenthone,[4] that the zero molecular rotation (and also the maximum of circular dichroism) occurs at a wave length greater by 60 to 110 Å. than the wave length of the maximum for the carbonyl absorption band. At least a slight shift in this direction may be noted in almost all the carbonyl compounds[5] thus far reported upon, although it is not so marked in the simpler ketones. This shift has been interpreted by some investigators[2,6] to mean an induced dissymmetry of the chromophore and a difference between the two carbon–oxygen valences. The use of rotatory dispersion curves in these cases shows therefore the non-homogeneity of an absorption band, or the fact that it is actually made up of two overlapping bands.

The present study was undertaken in order to collect further evidence concerning the carbonyl group by the use of a different cyclic ketone, 3-methylcyclohexanone,[7] simpler in structure than most of the carbonyl compounds previously used.

Previous determinations of the absorption spectrum of 3-methylcyclohexanone[8] were done

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[1] This work is included in a thesis submitted by Miss Naps to the Faculty of Wellesley College in partial fulfillment of the requirements for the degree of Master of Arts.

[2] Kuhn and Gore, *Z. physik. Chem.*, **B12**, 389 (1931).

[3] Lowry and French, *J. Chem. Soc.*, 2654 (1932).

[4] Lowry and Lishmund, *ibid.*, 709 (1935).

[5] Lowry and Gore, *Proc. Roy. Soc.* (London), **A135**, 13 (1932); Hudson, Wolfrom and Lowry, *J. Chem. Soc.*, 1179 (1933); Baldwin, Wolfrom and Lowry, *ibid.*, 696 (1935); Mathieu and Perrichtet, *Compt. rend.*, **200**, 1583 (1935); *J. phys. radium*, **7**, 138 (1936); Levene and Rothen, *J. Org. Chem.*, **1**, 116 (1936); *J. Chem. Phys.*, **4**, 48 (1936).

[6] Lowry and Walker, *Nature*, **113**, 565 (1924); Kuhn and Lehmann, *Z. Elektrochem.*, **37**, 549 (1931); Lowry, *ibid.*, **40**, 475 (1934); *Chemistry and Industry*, 477 (1935); Lowry and Allsopp, *Proc. Roy. Soc.* (London), **A146**, 313 (1934).

[7] This compound was kindly suggested to one of us by Professor T. M. Lowry of Cambridge University.

[8] Gelbke, *Jahrb. Radioakt. Elektronik*, **10**, 1 (1913); Henderson, Henderson and Heilbron, *Ber.*, **47**, 876 (1914); Purvis, *Proc. Cambridge Phil. Soc.*, **23**, 588 (1927).

either by the older Hartley-Baly method, or in solvents other than cyclohexane. Previous determinations of its rotatory power[9] have been carried out only for a limited number of wave lengths in the visible region of the spectrum. There have been no previous determinations of its rotatory dispersion in the ultraviolet.

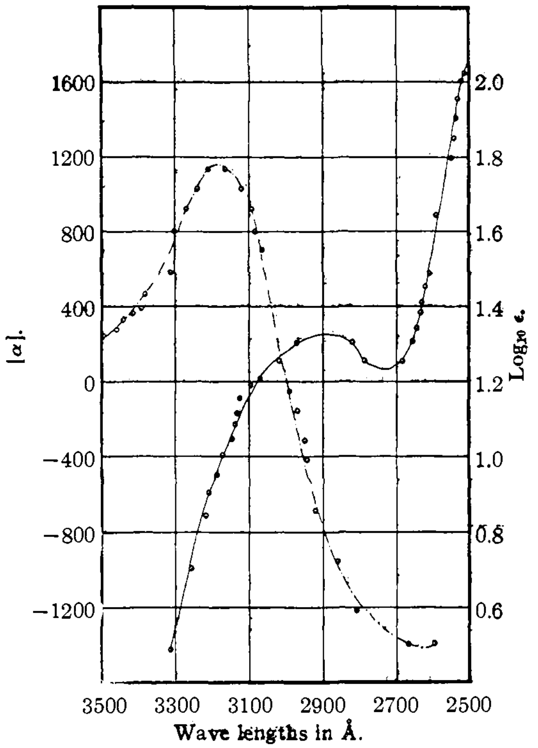

Fig. 1.—3-Methylcyclohexanone in cyclohexane: absorption spectrum, ————; rotatory dispersion, —·—·—·.

The method for obtaining the absorption spectrum data has already been described in a communication from this Laboratory.[10] The rotatory dispersion data were obtained by the same method used in a previous publication.[3] The ultraviolet polarimeter was a new instrument, but was made by Hilger according to Lowry's specifications, and no new method was involved.

The 3-methylcyclohexanone is readily obtained in its optically active form by the hydrolysis of naturally-occurring optically active pulegone, and it is easily purified through its bisulfite addition compound.[11] The cyclohexane solvent used in both determinations was purified by the usual method.[12]

The results are shown in Tables I and II and in the curves.

TABLE I

ABSORPTION SPECTRUM OF 3-METHYLCYCLOHEXANONE IN CYCLOHEXANE

Concn. (a) 0.1003 *M*; (b) 0.0501 *M*; (c) 0.0114 *M*

| | λ | $\text{Log}_{10}\,\epsilon$ | | λ | $\text{Log}_{10}\,\epsilon$ |
|---|---|---|---|---|---|
| (a) | 3355 | 0.30 | (b) | 2965 | 1.30 |
| (a) | 3310 | .48 | (b) | 2815 | |
| (a) | 3260 | .70 | (b) | 2660 | |
| (a) | 3220 | .84 | (b) | 2641 | 1.34 |
| (a) | 3210 | .90 | (b) | 2635 | 1.38 |
| (a) | 3185 | .95 | (b) | 2620 | 1.45 |
| (a) | 3170 | 1.00 | (b) | 2612 | 1.48 |
| (a) | 3145 | 1.04 | (c) | 2595 | 1.64 |
| (a) | 3135 | 1.08 | (c) | 2550 | 1.79 |
| (a) | 3130 | 1.11 | (c) | 2545 | 1.85 |
| (a) | 3125 | 1.15 | (c) | 2539 | 1.90 |
| (a) | 3095 | 1.18 | (c) | 2535 | 1.95 |
| (b) | 3065 | 1.20 | (c) | 2515 | 2.02 |
| (b) | 3015 | 1.25 | (c) | 2499 | 2.06 |
| (b) | 2785 | | (c) | 2488 | 2.09 |
| (b) | 2678 | | (c) | 2470 | 2.12 |

TABLE II

ROTATORY POWER OF 3-METHYLCYCLOHEXANONE IN CYCLOHEXANE

Concn.: (a) 0.0928 g. per cc.; (b) 0.0093 g. per cc.; (c) 0.00093 g. per cc.; (d) 0.00037 g. per cc.; (e) 0.00019 g. per cc.

| | λ | [α] | | λ | [α] |
|---|---|---|---|---|---|
| (a) | 4447 | 45.7 | (b) | 3314 | 564.5 |
| (a) | 4118 | 67.2 | (c) | 3068 | 689.6 |
| (a) | 4032 | 78.0 | (c) | 3076 | 797.1 |
| (a) | 4022 | 88.8 | (c) | 3306 | |
| (a) | 3878 | 99.6 | (c) | 3084 | 905.2 |
| (a) | 3786 | 121.1 | (c) | 3271 | |
| (a) | 3737 | 131.9 | (c) | 3116 | 1013.0 |
| (a) | 3704 | 142.7 | (c) | 3239 | |
| (a) | 3646 | 164.2 | (c) | 3166 | 1120.5 |
| (a) | 3609 | 175.0 | (c) | 3212 | |
| (a) | 3595 | 185.8 | (c) | 2987 | −64.7 |
| (a) | 3546 | 207.3 | (d) | 2965 | −161.7 |
| (a) | 3521 | 218.1 | (e) | 2948 | −323.3 |
| (a) | 3497 | 239.7 | (d) | 2941 | −431.0 |
| (a) | 3458 | 261.2 | (d) | 2918 | −700.5 |
| (b) | 3445 | 327.6 | (d) | 2852 | −969.8 |
| (b) | 3413 | 349.1 | (d) | 2805 | −1239.6 |
| (b) | 3393 | 370.7 | (e) | 2667 | −1401.0 |
| (b) | 3380 | 456.8 | (e) | 2598 | |

As expected, the positive and negative maxima of rotation occur approximately at the wave lengths corresponding to the half-width of the absorption band. The zero rotation is at 2970 Å., while the maximum of absorption is at 2890 Å. ($\log_{10} \epsilon = 1.34$). The zero rotation is thus displaced 80 Å. toward the red end of the spectrum.

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(9) Wallach, *Ann.*, **332**, 337 (1904); Tschugaeff, *Z. physik. Chem.*, **76**, 469 (1911); Rupe and Kambli, *Ann.*, **459**, 195 (1927); Tschugaeff and Chesno, *Trans. Sci. Chem. Pharm. Inst. (Moscow)*, No. 19, 181 (1928).

(10) Acly and French, THIS JOURNAL, **49**, 847 (1927).

(11) Rupe and Glenz, *Ann.*, **436**, 202 (1924); Rupe and Kambli, *ibid.*, **459**, 206 (1927).

(12) Lowry and Hudson, *Trans. Roy. Soc.* (London), **A232**, 126 (1933).

There is therefore by this study added one more bit of evidence for the induced dissymmetry of the carbonyl group, and for the non-homogeneous nature of its absorption band.

Work is being continued along the same lines in this Laboratory on other cyclic ketones, and on similar compounds involving doubly-bound oxygen.

## Summary

Tables and curves are given for the ultraviolet absorption and rotatory dispersion of 3-methylcyclohexanone in cyclohexane solution. These afford further evidence for the non-homogeneous nature of the carbonyl absorption band, and for the induced dissymmetry of the carbonyl group.

WELLESLEY, MASS. RECEIVED SEPTEMBER 15, 1936

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[FROM THE LABORATORY OF BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY SCHOOL OF MEDICINE]

# The Oxidation–Reduction Potentials of Derivatives of Thioindigo. I. Thioindigo Tetrasulfonate

BY PAUL W. PREISLER AND LOUIS H. HEMPELMANN

Until the mathematical formulation of the potential changes of the two-step oxidation–reduction process, involving one electron per step, by Michaelis[1] and by Elema,[2] resulting from their work upon the natural pigment pyocyanine, the potentials of all organic oxidation–reduction systems previously measured, which required two electrons per molecule for reduction, were considered to be one-step processes involving a pair of electrons.

Sullivan, Cohen and Clark,[3] who originally investigated systems of indigo sulfonate–leuco indigo sulfonate, considered these to be of the one-step two-electron class. Preisler and Shaffer[4] found that in the *p*H range of 10 to 12, red intermediate colors were formed, between the blue colors of the oxidants of indigo sulfonates and the yellow colors of the fully reduced reductants, when the oxidants were reduced by gradual addition of sodium hydrosulfite. A determination of the oxidation–reduction potentials in alkaline buffers revealed that these systems exhibited the characteristics of a two-step process.

An investigation of the potentials of simple and substituted sulfonates of the closely related thioindigo[5] is being conducted, to ascertain whether these exhibit the two-step oxidation–reduction process, to obtain further information on the nature of intermediary reduction products, and to study the effects of substitution on the potentials.

Since the initiation of this work, Remick[6] has reported on the potentials of thioindigo disulfonate and its reduction product and has concluded that his results with this compound show "... that the dye underwent a dimolecular reduction, involving but one electron per molecule of dye. The experimental data conform with the following mathematical formulation and establish this as the first system observed to undergo a thermodynamically reversible, dimolecular, oxidation–reduction reaction. No evidence of a second step was found." His mathematical formulation is developed on the assumption that this type of chemical reaction occurs.

This unusual interpretation of the thioindigo–leuco thioindigo system prompts the presentation at this time of results of work on the potentials of thioindigo tetrasulfonate, a representative derivative, which have been found to follow the same general mathematical formulations to which other previously studied organic systems seem to conform.

The potentials of the thioindigo tetrasulfonate–leuco thioindigo tetrasulfonate mixtures in acidic buffers of *p*H below 3 give typical curves approaching in shape those of a one-step two-valent process and in buffers of *p*H above 10.5 give curves showing transition into the shapes characteristic of the two-step process. In the *p*H range below 3, the $E_0'$–*p*H curve of the system oxidant–semiquinone lies in a region of more negative potential, and the $E_0'$–*p*H curve of the system semiquinone–reductant in a region of more positive potential, than that of the resultant oxidant–reductant curve; in the *p*H range above 10.5 the relative

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[1] L. Michaelis, *J. Biol. Chem.*, **96**, 703 (1932).

[2] B. Elema, *Rec. trav. chim. Pays-Bas*, **50**, 807, 1004 (1931); *J. Biol. Chem.*, **100**, 149 (1933).

[3] M. X. Sullivan, B. Cohen and W. M. Clark, *U. S. Public Health Reports*, **38**, 1669 (1923).

[4] P. W. Preisler and P. A. Shaffer, abstracts of papers presented at the American Chemical Society meeting, Chicago, Ill., 1933 (manuscript in preparation).

[5] P. Friedländer, *Ber.*, **39**, 1060 (1906); *Ann.*, **351**, 410 (1907).

[6] A. E. Remick, THIS JOURNAL, **58**, 733 (1936).