The identity of the products obtained by these procedures was established by mixed melting points. The purified compound melted at 237–237.5°.

Anal. Calcd. for $C_{32}H_{25}O_2N$: C, 84.4; H, 5.5; mol. wt., 455. Found: C, 84.2, 84.1; H, 5.6, 5.5; mol. wt. (Rast), 426.

Ethyl ε-Benzoyl-γ-cyano-β,γ,δ-triphenylcaproate (XII).—This compound was isolated on concentration and cooling of the alcohol filtrate from the crystallization of the β-diketone in (2c); yield of crude product (m. p. 135–140°), 6.4 g.; m. p. after recrystallization from ethyl alcohol, 142–143°.

Anal. Calcd. for $C_{34}H_{31}O_3N$: C, 81.4; H, 6.2. Found: C, 81.5; H, 6.3.

Hydrolysis of 3-Benzoyl-4-keto-1,2,6-triphenylcyclohexanenitrile (XIII). (1) In Alkaline Medium.—A solution of 35 cc. of methyl alcohol, 7 g. of potassium hydroxide, and 1 g. of the β-diketone XIII was placed in an ice-bath for thirty hours. The mixture was then treated with a large volume of water and extracted with ether. Acidification of the aqueous layer precipitated 0.4 g. of crude β-cyano-β,γ-diphenylbutyric acid, formed evidently by a reversal of the Michael condensation.

(2) **In Acid Medium.**—A mixture of 1.5 g. of the β-diketone XIII, 10.5 cc. of glacial acetic acid, and 10.5 cc. of constant boiling hydriodic acid was refluxed for one and one-half hours, during which a gradual solution of the diketone occurred. The acid was then neutralized with sodium carbonate, and the mixture was extracted with benzene. Evaporation of the benzene yielded 1.1 g. of the ketone VIII. The identity of the product and that of the oxime formed from it were established by mixed melting points with samples of these compounds prepared from the β-keto ester VI.

Summary

1. Benzyl cyanide and dibenzalacetone condense readily in the presence of a small amount of sodium methylate to form two γ-cinnamoyl-α,β-diphenylbutyronitriles and a 4-keto-1,2,6-triphenylcyclohexanenitrile.

2. Ethyl 3-cyano-6-keto-2,3,4-triphenylcyclohexanecarboxylate obtained by condensation of benzyl cyanide and ethyl cinnamate yields on ketonic hydrolysis a stereoisomer of the 4-keto-1,2,6-triphenylcyclohexanenitrile formed from benzyl cyanide and dibenzalacetone.

3. Condensation of ethyl γ-cyano-β,γ-diphenylbutyrate with benzalacetophenone and condensation of γ-benzoyl-α,β-diphenylbutyronitrile with ethyl cinnamate yield the same 3-benzoyl-4-keto-1,2,6-triphenylcyclohexanenitrile. The 4-keto-1,2,6-triphenylcyclohexanenitrile formed on hydrolysis of this β-diketone is identical with that produced by hydrolysis of the ethyl 3-cyano-6-keto-2,3,4-triphenylcyclohexanecarboxylate.

ROCHESTER, NEW YORK RECEIVED AUGUST 5, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WELLESLEY COLLEGE]

A Study of the Configuration of the Nickel Salt of Formyl Camphor

BY H. S. FRENCH AND G. CORBETT[1]

Nickel lends itself especially well to a study of the configuration of its coördination compounds. In common with several other metals, it may have either a square coplanar or a tetrahedral non-coplanar arrangement of bonds in its four coördination number complex. In asymmetric optically active complexes, the metal can be a center of asymmetry, or of optical activity, only in the case of the tetrahedral non-coplanar arrangement of its bonds. Any experimental procedure, therefore, which determines the group governing the optical activity of a molecule determines at the same time the arrangement of bonds around the metallic atom. Pfeiffer[2] and his co-workers recently used the determination of rotatory dispersion as such an experimental procedure, and assumed that the appearance of a Cotton effect indicated the tetrahedral bond arrangement and *vice versa*. Because the rotatory dispersion was determined only for a relatively small portion of the visible region of the spectrum, and because no correlation was made with absorption spectra, inconsistent and unexplainable conclusions resulted. We present therefore in this paper further experimental results on one of the same compounds used by Pfeiffer, namely, the ultraviolet absorption spectrum and the ultraviolet rotatory dispersion of *d*-nickel formyl camphor. Our conclusion for this compound is the opposite from Pfeiffer's conclusion. He found no Cotton effect and therefore concluded that the nickel complex in nickel formyl camphor

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

[2] Pfeiffer, Christelheit, Hesse, Pfitzner and Thielert, *J. prakt. Chem.*, **150**, 261 (1938).

has the square, coplanar configuration. We find that the experimental rotatory dispersion in both the visible and ultraviolet regions is practically identical with the theoretical rotatory dispersion calculated from the absorption band produced by the nickel center in the molecule. The rotatory power of the molecule is therefore governed almost completely by the nickel center, and therefore the nickel complex is tetrahedral non-coplanar.

Confirmation of this conclusion is found in the following facts and results. Among the metals which may form either of these two configurations nickel is unique in that it is diamagnetic when it has the square coplanar configuration, and exhibits a fairly high paramagnetism when it has the tetrahedral configuration. It has no unpaired electrons in its square coplanar configuration and it has two unpaired electrons in its tetrahedral configuration. Pauling[3] explains how the configuration depends upon the orbitals which enter into hybridization, and this hybridization determines the number of unpaired electrons. We have tested the magnetic susceptibility of nickel formyl camphor both in the solid state and in methyl alcohol solution, and find that it is strongly paramagnetic.

The tetrahedral non-coplanar configuration for nickel formyl camphor is therefore established. The reciprocal confirmations of this fact would seem to put on an even firmer footing than before both methods used in the determination, namely, the application of the relation between absorption spectra and rotatory dispersion, and the magnetic susceptibility method for determining hybrid bonds.

Since Pauling[4] states that "the factors which determine whether the diamagnetic square or the paramagnetic tetrahedral configurations will be assumed by a nickel complex cannot be stated precisely," we are continuing in this Laboratory work on the magnetic susceptibility of nickel compounds, in the hope that more definite information may be gathered upon which to make generalizations. A recent paper by Tyson and Adams[5] gives magnetic data on two further nickelous complexes, and shows nickel disalicylaldehyde paramagnetic and tetrahedral, while nickel disalicylaldimine is diamagnetic and square coplanar.

Experimental Part

Preparation of Nickel Formyl Camphor.—*d*-Formyl camphor was first prepared from *d*-camphor, sodium, and amyl formate by the method of Claisen.[6] The nickel salt of formyl camphor was prepared as described by Pfeiffer[1] from formyl camphor and nickel acetate in methyl alcohol solution.

Anal. Calcd. for $(C_{11}H_{15}O_2)_2Ni \cdot 2H_2O$: Ni, 12.96. Found[7]: Ni, 12.94 and 12.89.

Absorption Spectra.—The method used is the same as in recent communications from this Laboratory.[8] The results are shown in Table I, and in Curve A in Fig. 1. From the experimental curve A for the absorption, the band due to the nickel complex was analyzed for the theoretical band B by the use of the Lowry–Hudson[9] equation

TABLE I

ABSORPTION SPECTRUM OF *d*-NICKEL FORMYL CAMPHOR IN METHYL ALCOHOL

Concn. 0.0000525 *M*; length of cell (a) 4 cm., (b) 1 cm.

λ	$\log_{10}\epsilon$	λ	$\log_{10}\epsilon$
3470	2.68 (a)	3354 2928 2704 2636	3.68 (a)
3436 2387	2.98 (a)	3348 2942	3.72 (a)
3421 2394	3.16 (a)	3338 2964	3.76 (a)
3419 2404	3.28 (a)	3334 2984	3.80 (a)
3400 2428	3.38 (a)	3320 2996	3.83 (a)
3392 2487	3.46 (a)	3319 3010	3.86 (a)
3380 2867 2810 2509	3.53 (a)	3302 3032	3.89 (b)
3370 2894 2788 2533	3.58 (a)	3262 3072	3.98 (b)
3360 2912 2739 2591	3.64 (a)	3236 3090	4.06 (b)
		—	4.15 (b)

$$2.303 \log_{10} \frac{\epsilon_{\text{max.}}}{\epsilon} = \left(\frac{\lambda - \lambda_0}{\theta}\right)^2$$

By averaging three values of θ calculated from experimental points, a value of θ was obtained which was then used in calculating points for the

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[3] Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 111.

[4] Pauling, *Ibid.*, p. 112.

[5] Tyson and Adams. THIS JOURNAL, **62**, 1228 (1940).

[6] Bishop, Claisen and Sinclair, *Ann.*, **281**, 331 (1894).

[7] Acknowledgment is made to Miss Phyllis Ambler for this analysis.

[8] French and Gens, THIS JOURNAL, **59**, 2600 (1937).

[9] Hudson, Wolfrom and Lowry, *J. Chem. Soc.*, 1179 (1933).

theoretical curve. Table II shows the calculated values.

TABLE II

CALCULATED POINTS FOR THE THEORETICAL ABSORPTION BAND OF *d*-NICKEL FORMYL CAMPHOR IN METHYL ALCOHOL

$\text{Log}_{10}\epsilon_{\text{max.}} = 4.10$ at 3172 Å.; $\theta = 184.9$ Å.

λ	$\text{Log}_{10}\epsilon$	λ	$\text{Log}_{10}\epsilon$
3509 2835	2.66	3359 2985	3.66
3480 2864	2.90	3327 3017	3.80
3453 2891	3.10	3285 3059	3.94
3417 2927	3.34	3242 3102	4.04
3390 2954	3.50		

Rotatory Dispersion.—The rotatory dispersion data were obtained by the same method previously used in this Laboratory.[8] The results are shown in Table III and as curve C in Fig. 1. By plotting $1/[M]$ against λ^2 a straight line was obtained which crossed the axis of $\frac{1}{[M]} = 0$ at λ^2 10,000,000 or $\lambda = 3162$ Å., almost the head of the absorption band (at 3172 Å.) of the nickel center of the molecule. This is evidence, according to Lowry,[10] that the optical activity of the molecule is governed almost wholly by this absorption band at 3172 Å., and that there is practically no contribution from the band at the shorter wave length.

TABLE III

ROTATORY POWER OF *d*-NICKEL FORMYL CAMPHOR IN METHYL ALCOHOL

Concn.: (a) 0.00211 g. per cc.; (b) 0.002099 g. per cc.; (c) 0.002125 g. per cc.; (d) 0.0002125 g. per cc.

	λ	$[M]^{23°}$	$[M]$ calcd.
(a)	4967	1900	1900
(b)	4825	2126	2091
(b)	4700	2331	2300
(b)	4537	2547	2711
(b)	4453	2752	2862
(b)	4408	2970	3057
(b)	4357	3182	3217
(c)	4297	3283	3423
(c)	4193	3710	3841
(c)	4110	4136	4259
(c)	4045	4541	4638
(d)	3885	6396	5946
(d)	3805	8102	6839
(d)	3717	9809	8269
(d)	3628	11520	10430
	3326	. . .	29720

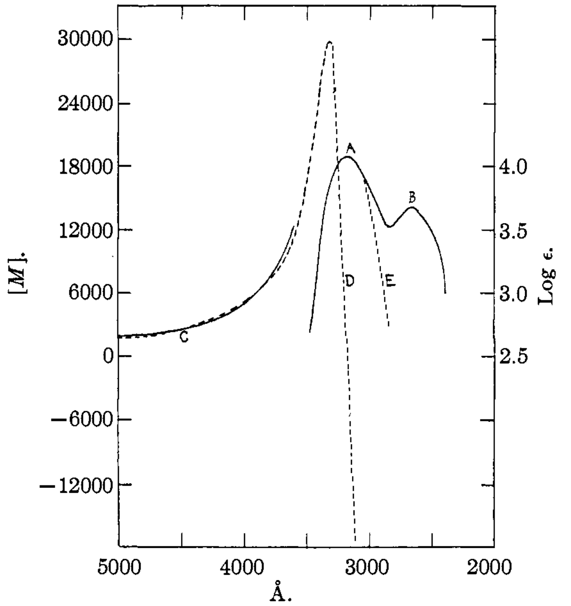

Fig. 1.—Nickel formyl camphor: AB, obsd. absorption spectrum; AE, calcd. absorption band; C, obsd. rotatory dispersion; D, calcd. rotatory dispersion governed by band AE.

The theoretical curve for the rotatory dispersion governed by the absorption band at 3172 Å. was calculated by the use of two different equations. For wave lengths near the absorption region, where the Cotton effect becomes operative, the Lowry–Hudson[9] equation was used

$$[M]_\lambda = \frac{[\phi]}{m}\frac{\lambda_\phi}{\lambda}\left[e-(\lambda-\lambda_0/\theta)^2\int_0^{(\lambda-\lambda_0)/\theta} e^{x^2}\mathrm{d}x + \frac{\theta}{2\,(\lambda+\lambda_0)}\right]$$

For wave lengths well outside the absorption region the simpler Natanson[11] equation was applied

$$[M]_\lambda = \frac{A(\lambda^2-\lambda_0^2)}{(\lambda^2-\lambda_0^2)^2+\lambda^2\lambda_1^2}$$

$[M]_\lambda$ is the partial molecular rotation at wave length λ, m is the maximum value of the terms inside the bracket, $[\phi]$ is the maximum value of $[M]$ which occurs at wave length λ_ϕ, λ_1 is the half-width of the absorption band, λ_0 is the wave length of maximum of absorption. λ_ϕ is obtained by subtracting $\lambda_1/2$ from λ_0. θ is the half-width (λ_1) divided by a constant 1.6651. A is a constant obtained by using experimental values of $[M]_\lambda$ at wave lengths as far as possible from the region of absorption. The values of $[M]_\lambda$ for the calculated rotary dispersion curve are given in the third column of Table III, and the curve is shown as D in Fig. 1.

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(10) Lowry and Owen, *Trans. Faraday Soc.*, **36**, 373 (1930).

(11) Natanson, *Acad. Sci. Cracow*, Bull. No. 8, p. 764 (1908).

Magnetic Susceptibility.—The method of Gouy[12] was used, and the nickel formyl camphor proved to be definitely paramagnetic. The details of the method and the quantitative value of the molecular magnetic susceptibility (approximately 2500×10^{-6}) will be given in a forthcoming paper on the magnetic susceptibilities of several nickel salts.

Summary

New data are presented on the ultraviolet absorption spectrum and ultraviolet rotatory dispersion of nickel formyl camphor. The conclusion is drawn that the configuration of the nickel complex is tetrahedral and not square coplanar. The conclusion is confirmed by the evidence that the compound is paramagnetic.

Wellesley, Mass. Received September 17, 1940

[12] Gouy, *Compt. rend.*, **109**, 935 (1889).

[Contribution from the Department of Chemistry of The Johns Hopkins University]

A Study of the Catalytic Properties of Beryllium Chromite

By R. K. Ladisch[1] and J. C. W. Frazer

In work previously reported[2] from this Laboratory, beryllium chromite was found to be a catalyst for the oxidation of carbon monoxide. An effort was made to measure the adsorption of oxygen by beryllium chromite but the amount of oxygen adsorbed increased with each succeeding run. It was thought that the alternate oxidation and reduction involved in the adsorption of the oxygen and the subsequent preparation of the catalyst for a succeeding run activated it.

The present work was undertaken to find the limit to which beryllium chromite could be activated by alternate oxidation and reduction. It was found that the increasing adsorption of oxygen took place only on catalysts that were washed with distilled water after decomposition of the original compound and not on unwashed catalysts. The unwashed catalyst was found to have a definite composition and was reproducible; so it was studied in greater detail. (A study of the washed catalyst is now in progress.)

By decomposition of double beryllium ammonium chromate, beryllium dichromate was formed quantitatively. This was quantitatively reduced to chromite by hydrogen. This observation is of importance because it shows that the readily available beryllium dichromate can be used as a catalyst after reduction instead of a chromite made by thermal decomposition of double beryllium ammonium chromate.

Experimental

Beryllium chromite catalyst was made by thermal decomposition of the double beryllium ammonium chromate, $Be(NH_4)_2(CrO_4)_2$, and subsequent reduction. The double salt was heated in a balloon flask, raising the temperature to 175° at the rate of a few degrees per hour. Slow decomposition began at 175° and was complete at 250°. A vacuum was maintained in the flask by means of a mechanical oil pump.

The product of the thermal decomposition of the double salt was completely soluble in 2% hydrochloric acid except for a few white, flocculent particles. Three samples of the product were analyzed according to the method of Moser and Singer.[3] Samples 1 and 2 contained some residual water from the decomposition. Sample 3 was heated to 1000° for one hour. These samples gave values very close to the correct analysis for beryllium dichromate.

Anal. Calcd. for $BeCr_2O_7$: BeO, 11.1; Cr_2O_3, 67.6. Found: Sample 1, BeO, 10.8; Cr_2O_3, 65.7; Sample 2, BeO, 10.8; Cr_2O_3, 62.8; Sample 3, BeO, 11.5; Cr_2O_3, 67.7.

X-Ray diffraction spacings were obtained from powder photographs which were taken using unfiltered molybdenum radiation. No lines were obtained from the sample of catalyst heated in air to 250° for one hour. Samples of catalyst heated to 300° for forty hours, to 500° for five

Table I

No. of line	Intensity	Spacing in Å.
1	Strong	4.01
2	Strong	3.26
3	Weak	2.60
4	Weak	2.41
5	Weak	2.28
6	Weak	2.12
7	Weak	2.02
8	Weak	1.69
9	Strong	1.64
10	Weak	1.39

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[1] Condensed from a dissertation presented to the faculty of The Johns Hopkins University in partial fulfillment of the requirement for the M.A. degree in Chemistry. Original manuscript received October 23, 1939.

[2] Heard and Frazer, *J. Phys. Chem.*, **42**, 855 (1936).

[3] Moser and Singer, *Monatsh.*, **48**, 673 (1927).