and, in order to find out whether it also was square planar and hence an example of a high-spin square complex of Co(II)[2], a single crystal X-ray study was undertaken.

It was found that Co(DPM)$_2$ crystallizes in space group I4$_1$/a with four molecules per unit cell. This requires that the Co atoms lie on $\bar{4}$ axes which in turn requires that the CoO$_4$ configuration be such that one CoO$_2$ set lies in a plane perpendicular to that defined by the other CoO$_2$ set. Although the O-Co-O angles may deviate somewhat from the tetrahedral angle, it can be said that the coördination of Co in this compound is "tetrahedral" in the usual, somewhat loose usage of that term. It does not seem likely that there will be large deviations from the tetrahedral angle in view of the dimensions and configuration of the ligands. Zn(DPM)$_2$ is isomorphous with Co(DPM)$_2$ and mixed crystals may be grown. An e.s.r. study of Co(DPM)$_2$ in a dilute mixed crystal is in progress and will be reported later.

This result was surprising since Co(DPM)$_2$ has a reddish color reminiscent of the colors of non-tetrahedral Co(II) complexes[2] but not at all like the deep blue and green hues of the previously known tetrahedral ones.[3] Moreover, the visible absorption band of Co(DPM)$_2$ has an $\epsilon_{\max}$ of only 40 and this is much closer to those (~10) found in octahedral complexes and others not previously thought to be tetrahedral than to those (400–1700) of previously known tetrahedral complexes.

Rigorous theoretical treatment of the oscillator strengths $f(\nu_i)$ of electronic transitions in tetrahedral complexes is a very formidable task which has not yet been accomplished, but Ballhausen and Liehr,[4] in semiquantitative calculations, have provided convincing evidence that the intensities are direct functions of the degree of mixing of ligand orbitals and metal *d* orbitals and, considering only MO's of σ type, they produced an expression for this relationship. Moreover, it is well-known that the Racah parameter B is decreased from the free ion value in tetrahedral Co(II) complexes[3] and in complexes generally[5,6,7] and one[8] likely cause for this is mixing of ligand and metal orbitals resulting in delocalization of metal *d* electrons. From these considerations one might expect a correlation between absorption band intensities and the amount of lowering, ΔB, of the B value from the free ion value (967 cm.$^{-1}$ for Co(II)).

The spectrum of Co(DPM)$_2$ therefore was measured and from the positions of the ν_3 and ν_2 bands a B value of 880 cm.$^{-1}$ was calculated.[3] Thus ΔB = 87 cm.$^{-1}$, which is very much smaller than ΔB values (200–300 cm.$^{-1}$) previously[3] found in tetrahedral Co(II) complexes.

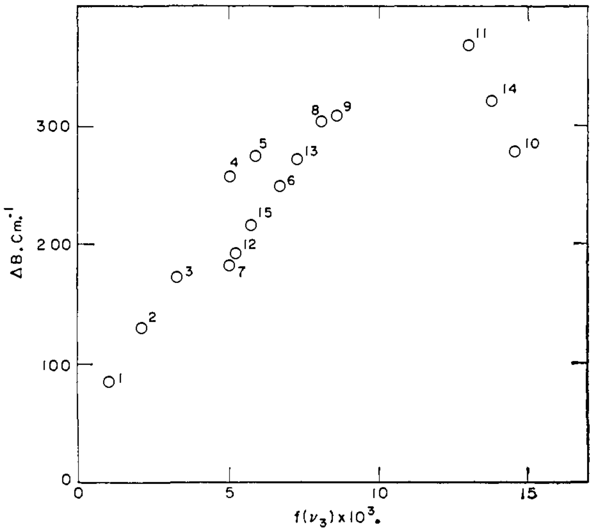

Fig. 1.—A plot of $f(\nu_3)$ *vs.* ΔB for all tetrahedral Co(II) complexes on which the necessary data are currently available. The compounds and, where appropriate, sources of data are: 1, Co(DPM)$_2$; 2,3, Co(Ph$_3$PO)$_2$(ONO$_2$)$_2$ and Co(Ph$_3$AsO)$_2$(ONO$_2$)$_2$, data from D. M. L. Goodgame, R. H. Soderberg and F. A. Cotton, *J. Chem. Soc.*, in press; 4, 5, 6, 7, 8, 9, 10, [CoCl$_4$]$^{2-}$, [CoBr$_4$]$^{2-}$, [Co(NCO)$_4$]$^{2-}$, [Co(Ph$_3$PO)$_4$]$^{2-}$, [CoI$_4$]$^{2-}$, [Co(N$_3$)$_4$]$^{2-}$, [Co(NCS)$_4$]$^{2-}$, data from ref. 3; 11, 12, Co in ZnS and ZnO, data from H. A. Weakliem, RCA Laboratories, private communication; 13, [Co(benzimidazole)$_4$]$^{2+}$, data from M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, in press; 14, [Co(NCSe)$_4$]$^{2-}$, data from F. A. Cotton, D. M. L. Goodgame and H. E. Haas, *Inorg. Chem.*, in press; 15, [Co(Ph$_3$AsO)$_4$]$^+$, data from D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *Inorg. Chem.*, in press.

In order to test further the expected relationship between ΔB and $f(\nu_3)$, previously published and newly obtained data for a number of other tetrahedral Co(II) complexes have been collected and plotted as shown in Fig. 1. It can be seen that there is a generally good correlation of the kind anticipated. Work along these lines is being continued and detailed reports will be submitted as soon as possible.

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[2] F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

[3] F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *ibid.*, **83**, 4690 (1961), and other references cited here.

[4] C. J. Ballhausen and A. D. Liehr, *J. Mol. Spect.*, **2**, 342 (1958); errata, *ibid.*, **4**, 190 (1960).

[5] C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 53 (1957).

[6] O. Bostrup and C. K. Jørgensen, *ibid.*, **11**, 1223 (1957).

[7] T. M. Dunn, *J. Chem. Soc.*, 623 (1959).

[8] As Dunn[7] points out, the situation actually is somewhat more complicated. Also it has been suggested[9] recently that configuration interaction under the influence of the ligand field may make some contribution to the lowering of the *B* values.

[9] H. B. Gray and C. J. Ballhausen, *Acta Chem.*, **15**, 1327 (1961).

[10] Alfred P. Sloan Foundation Fellow.

[11] National Science Foundation Predoctoral Fellow.

DEPARTMENT OF CHEMISTRY
AND LABORATORY OF CHEMICAL AND SOLID STATE PHYSICS
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS
F. A. COTTON[10]
R. H. SODERBERG[11]

RECEIVED JANUARY 22, 1962

HYDROGEN ION DEPENDENCE OF THE RATE OF REDUCTION OF ACETONE BY BOROHYDRIDE

Sir:

Recently H. C. Brown[1] has published additional data on the reduction of acetone by borohydrides in

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[1] H. C. Brown and K. Ichikawa, *J. Am. Chem. Soc.*, **83**, 4372 (1961).

unbuffered solutions showing that the rate is first order in both borohydride and acetone. We wish to report some preliminary data in aqueous solutions which were buffered. These data show that the rate of reduction of acetone by borohydride is zero order in hydrogen ion. Two aspects of the lack of hydrogen ion dependence for the acetone reaction are noteworthy. First, it might be considered unexpected since three out of four of the borohydride reactions previously reported are first order in hydrogen ion. The reaction with water,[2] the reaction with ferricyanide,[3] and the reaction with iodate[4] are first order in hydrogen ion while the reaction with permanganate[5] is zero order. Second, from a practical standpoint, if a borohydride reduction is carried out in a basic solution, less borohydride will be lost by hydrolysis. For example, at 25° in one hour at pH 9 over 90% of the borohydride will be lost by hydrolysis whereas at pH 13 (0.1 M OH^-) less than 0.1% will be lost.

At 25°, we found the second order specific rate constant ($sec.^{-1}$) for the borohydride–acetone reaction to be 2.7×10^2 at pH 13.0, 2.8×10^2 at pH 11.6, and 3.0×10^2 at pH 10.2. These values compare to 1.8×10^2 found in 0.5 M OH^- by Jensen,[6] 2.3×10^2 found in the same base concentration by Stockmayer,[2] and 3.2×10^2 (estimated from Brown's 0° value and Stockmayer's activation energy value) found in an unbuffered solution by H. C. Brown.

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[2] W. H. Stockmayer, R. R. Miller, and R. J. Zeto, *J. Phys. Chem.*, **65**, 1076 (1961).

[3] T. Freund, *J. Inorg. Nucl. Chem.*, **9**, 246 (1959).

[4] T. Freund and N. Nuenke, in press.

[5] T. Freund and N. Nuenke, *J. Am. Chem. Soc.*, **83**, 3378 (1961).

[6] E. H. Jensen, "A Study of Sodium Borohydride," Nyt Nordisk Forlag, Copenhagen, 1954.

CONVAIR SCIENTIFIC RESEARCH LAB. T. FREUND
SAN DIEGO 11, CALIFORNIA N. NUENKE

RECEIVED DECEMBER 26, 1961

OPTICAL ROTATORY DISPERSION STUDIES. LXIX.[1] THE ABSOLUTE CONFIGURATION OF THE 2-METHYLCYCLOHEXANOLS AND SOME OBSERVATIONS ON A TWIST FORM IN THE CONFORMATIONAL EQUILIBRIUM OF 2-METHYLCYCLOHEXANONE

Sir:

Both *cis*- and *trans*-2-methylcyclohexanols have been resolved by Kenyon and collaborators[2] but no assignments of absolute configuration have as yet been made to the optically active antipodes. The simplest solution to this problem appeared to us to be through optical rotatory dispersion measurements[3] and a successful method is described herewith.

Kenyon, *et al.*,[2] already have shown that (+)-*trans*-2-methylcyclohexanol (I)[4] and (−)-*cis*-2-methylcyclohexanol (IV) both lead to (+)-2-methylcyclohexanone, thus proving that these two diastereoisomers possess the same absolute configuration at the methyl-bearing asymmetric center. Using partially resolved material, we have confirmed that (+)-*trans*-2-methylcyclohexanol (I) affords (+)-2-methylcyclohexanone (positive Cotton effect), while (+)-*cis*-2-methylcyclohexanol (III) gives (−)-2-methylcyclohexanone (negative Cotton effect). By feeding racemic 2-methylcyclohexanone to rabbits, it has been possible to isolate from the urine pure (+)-*trans*-2-methylcyclohexanol (I) in the form of its methyl tri-O-acetyl-β-D-glucosiduronate (m.p. 157–158°, $[\alpha]^{23}{}_D$ −9.8° in chloroform), which was cleaved by acid to (+)-I, characterized as the 3,5-dinitrobenzoate, m.p. 126–127°, $[\alpha]^{25}{}_D$ +56.6° (chloroform).

Rapid oxidation of the biologically-resolved alcohol I with chromium trioxide in acetone solution—conditions which do not cause racemization of the adjacent asymmetric center[5]—provided optically pure (+)-2-methylcyclohexanone with a positive Cotton effect (peak: $[\alpha]^{MeOH}_{305}$ +515°; trough: $[\alpha]^{MeOH}_{265}$ −565°) of molecular amplitude (a) + 1210°, which remained unchanged for at least five days when kept in methanol solution.

Application of the octant rule[6] should now lead to a decision regarding the absolute configuration of this ketone, since the rule predicts a negligible Cotton effect for Ve and a strongly positive one for Va, the reverse applying to the enantiomers of V. It follows, therefore, that *the sign of the Cotton effect will be governed by the axial conformer* present in the equilibrium and in view of the observed positive Cotton effect, we can assign stereoformula V to (+)-2-methylcyclohexanone, which in turn leads to I–IV as the correct absolute configurational representations for (+)-*trans*-, (−)-*trans*-, (+)-*cis*- and (−)-*cis*-2-methylcyclohexanol, respectively.

While these qualitative conclusions result in an unambiguous absolute configurational assignment, quantitative considerations now can shed some light on the conformational equilibrium existing in 2-methylcyclohexanone, which hitherto has only been studied in more highly substituted systems.[7,8] By subtracting the molecular amplitude of the Cotton effect of (+)-2,2-5-trimethylcyclohexanone[9] from that of (+)-*trans*-2,5-dimethylcyclohexanone[10] one obtains[6] a value of a +5560°, which would represent the predicted molecular amplitude of the conformer Va. For the conformer Ve, we can assume $a \sim 0$, as judged from a comparison of the molecular amplitudes of (+)-3-methylcyclohexanone *vs.* (+)-*trans*-2,5-dimethylcyclohexanone or of cholestan-3-one (VI) *vs.* 2α-methylcholestan-3-one,[11] the introduction of the

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[1] Paper LXVIII, K. Mislow, M. A. W. Glass, Robert E. O'Brien, Philip Rutkin, David H. Steinberg, J. Weiss and Carl Djerassi, *J. Am. Chem. Soc.*, **84**, in press (1962).

[2] G. A. L. Gough, H. Hunter and J. Kenyon, *J. Chem. Soc.*, 2052 (1926).

[3] C. Djerassi, "Optical Rotatory Dispersion: Applications to Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1960.

[4] Absolute configurations according to the steroid notation.

[5] (a) C. Djerassi, E. J. Warawa, J. M. Berdahl and E. J. Eisenbraun, *J. Am. Chem. Soc.*, **83**, 3334 (1961); (b) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnkoff and D. Willner, *ibid.*, **83**, 3986 (1961); (c) G. Ohloff, J. Osiecki and C. Djerassi, *Ber.*, **95**, in press (1962).

[6] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

[7] W. Klyne, *Experientia*, **12**, 119 (1956).

[8] N. L. Allinger and H. M. Blatter, *J. Am. Chem. Soc.*, **83**, 994 (1961).

[9] C. Djerassi, J. Osiecki and E. J. Eisenbraun, *ibid.*, **83**, 4433 (1961).

[10] A. Melera, D. Arigoni, A. Eschenmoser, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **39**, 441 (1956).

[11] Newly determined values.