higher than that of its optically active components.

Since Grewe and Pachaly have proved their compound to have a 2,5-di-*O*-tosyl structure rather than the 4,5-di-*O*-tosyl structure that we had guessed for our compound, the latter may now be written with confidence as 1,3-*O*-benzylidene-2,5-di-*O*-*p*-tolylsulfonyl-D-arabitol. The analogous, partially tosylated 1,3-*O*-methylene-D-arabitol (m.p. 161–163°) to which we assigned tentatively a 4,5-di-*O*-tosyl structure, now appears more likely to be 1,3-*O*-methylene-2,5-di-*O*-*p*-tolylsulfonyl-D-arabitol.

Experimental

1,3-*O*-Benzylidene-2,5-di-*O*-*p*-tolylsulfonyl-DL-arabitol.—About 0.15 g. of each enantiomorph was dissolved in 5 ml. of chloroform, and the mixture diluted with *n*-pentane as the racemate began to crystallize in clusters of needles. After two recrystallizations from chloroform–pentane and one from ethanol, the product melted at 152–154° and showed no detectable rotation in chloroform (*c* 0.8, *l* 4).

Anal. Calcd. for $C_{26}H_{28}O_9S_2$: C, 56.92; H, 5.14; S, 11.69. Found: C, 56.77; H, 4.88; S, 11.71.

Acknowledgment.—The authors wish to thank Dr. William C. Alford and his associates for the microanalyses, Mr. William M. Jones for the infrared data, and Mr. Vernon M. Mosley and Dr. Norman E. Sharpless, all of this Institute, for the X-ray data.

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COMMUNICATIONS TO THE EDITOR

THE STABILITIES OF 1,3,5-TRINITROBENZENE COMPLEXES OF ORTHO SUBSTITUTED BIPHENYLS

Sir:

X-Ray diffraction studies of crystalline 1:1 complexes of aromatic substances with 1,3,5-trinitrobenzene or benzoquinone, both of which seem to function as electron acceptors in the interactions, show that the acceptor molecule is oriented in the complex with its ring plane parallel to and separated by somewhat over 3 Å. from the plane of the donor ring.[1] Studies are in progress in this Laboratory to test whether or not the attainment of this parallel plane configuration by the complex components is highly critical for the achievement of maximum complex stability.

A clearly positive answer to this question has now been obtained through the evaluation of equilibrium constants for formation of 1:1 complexes of a series of methyl substituted biphenyls with 1,3,5-trinitrobenzene in carbon tetrachloride at 25°. These were determined through colorimetric investigation in the 340–415 mμ region, in which the complexes show characteristic absorption, of a series of solutions in which the biphenyl concentrations varied from 0.05–0.5 *M* and the concentration of the nitro compound ranged from 10^{-3} to 10^{-4} *M*.[2] The equilibrium constant, K_1 (see equation 1) measured for the complex of

$$K_1 = (\text{complex})/(\text{biphenyl})\,(\text{TNB}) \qquad (1)$$

biphenyl itself was 0.92 mole^{-1} l. The corresponding constants for the isomeric monomethyl biphenyls were 0.35 (ortho), 1.38 (meta) and 1.70 (para). For symmetrically substituted dimethylbiphenyls values of 0.34 (*o,o'*), 1.65 (*m,m'*) and 2.40 (*p,p'*) were obtained, and for bimesityl K_1 was <0.1.

The electronically favorable effects of methyl substituents on complex stabilities,[3] which are apparent in the K_1 values for the *m*- and *p*-substituted donors, are obviously negated when those substituents are so placed that they offer steric inhibition to the assumption of a coplanar configuration by the two rings of the donor molecule. This steric effect is manifested by even a single ortho substituent and is extreme in the case of bimesityl.[4]

It seems likely that 1,3,5-trinitrobenzene in a 1:1 complex with biphenyl would interact strongly with only one ring of the donor. Apparently, then, in a hindered biphenyl type donor one phenyl group, through interference with the nitro groups which protrude from the perimeter of the acceptor ring, forces the acceptor out of a favorable parallel orientation to the ring with which it is interacting or forces a wider separation between the donor and acceptor rings than is favorable to the interaction. It seems doubtful, in the case of those ortho substituted biphenyl molecules which have actually coördinated with *s*-trinitrobenzene, that the two rings of the donor can have been forced into a coplanar configuration. This would require that the heats of formation of complexes of hindered and unhindered biphenyls would differ by rather large amounts (possibly by as much as the energy of activation reported for the racemization of an optically active biphenyl[5]), and there is

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[1] (a) H. M. Powell and G. Huse, *J. Chem. Soc.*, 435 (1943); (b) J. S. Anderson, *Nature*, **140**, 583 (1937).

[2] The method is essentially that used to measure stabilities of other colored complexes of aromatic substances in solution; *cf.* L. J. Andrews and R. M. Keefer, THIS JOURNAL, **75**, 3776 (1953); S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, *ibid.*, **76**, 69 (1954).

[3] L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

[4] It is significant that only those ortho substituted biphenyls in which the substituents are small enough to offer no hindrance to coplanarity of the donor rings form crystalline complexes with 2,4,7-trinitrofluorenone. There is also evidence that the stabilities of complexes of this acceptor with 1-cyclohexenyl- and 1-cyclopentenylnaphthalenes are reduced by the presence of methyl substituents at ortho positions in the cycloalkenyl rings; *cf.* C. B. Coleman, Abstracts of Papers Presented at Minneapolis, Minn., Division of Organic Chemistry, American Chemical Society, Sept., 1955; L. H. Klemm, J. W. Sprague and H. Ziffer, *J. Org. Chem.*, **20**, 200 (1955).

[5] R. L. Shriner, R. Adams and C. S. Marvel in "Organic Chemistry," Vol. I, edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 357.

abundant evidence that the heats of donor acceptor type interactions are generally small in value and do not vary widely with changes in component structure.[3]

Further work on the heats of formation of these complexes is under way. The authors are indebted to the National Science Foundation for a grant in support of this research.

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RESOLUTION AND MUTAROTATION OF *cis*-NITRITO-NITRO-BIS-(ETHYLENEDIAMINE)-COBALT(III)

Sir:

It previously has been demonstrated[1] that the nitrite ion can attach itself to the inner coördination sphere of a cobalt ion in two ways: through an oxygen (Nitrito) or through the nitrogen (Nitro). The conversion of the nitrito form to the nitro takes place rapidly and completely in solution or in the solid state with little or no *cis–trans* interconversion. The mechanism of this reaction is of especial interest since it may provide valuable information on the mode of substitution in coördination compounds.

In connection with a study of the mechanism of the formation of nitrito compounds and of the nitrito-nitro conversion, we have recently succeeded in resolving *cis*-$[Co(en)_2(NO_2)(ONO)]^+$ by the use of ammonium *d*-α-bromocamphor-π-sulfonate, (*d*-NH_4BCS), and a partial resolution has been achieved with active powdered quartz. This is believed to be the first reported isolation of a nitrito complex in optically active form.

The resolution was achieved by the addition of a slight excess of solid *d*-NH_4BCS to a saturated solution of *cis*-$[Co(en)_2(NO_2)(ONO)]ClO_4$ at 0°. Reddish-yellow needles were deposited, which were dissolved in water at 0° and recrystallized by the addition of solid *d*-NH_4BCS. The crystals were washed with ice-cold acetone and dried under vacuum: (I) *d-cis*-$[Co(en)_2(NO_2)(ONO)]$*d*-BCS, $[\alpha]^{18}\text{D}$ +81°.[2] The resolving agent was removed by triturating the diastereomer with a saturated solution of sodium perchlorate at 0° and washing the precipitated powder with ice-cold ethanol. Recrystallization was accomplished by solution in cold water and addition of solid sodium perchlorate. The orange crystals were freed of sodium perchlorate by washing with ice-cold ethanol and dried under vacuum: (II) *d-cis*-$[Co(en)_2(NO_2)(ONO)]ClO_4$, $[\alpha]^{18}\text{D}$ + 62.3°[2]. *Anal.* Calculated for $CoC_4H_{16}N_6O_8Cl$; Co, 15.92; C, 13.02; H, 4.33; N, 22.76. Found: Co, 15.61; C, 13.13; H, 4.42; N, 22.58. Since conversion to the nitro form takes place rapidly, the resolved compounds were used immediately.

Absorption spectra and molecular rotation were used to demonstrate that the resolved products were the nitrito form. The molecular extinction coefficients (extrapolated) of compounds I and II are exactly the same as for the known inactive compounds and quite different from the dinitro compounds. The compounds *d-cis*-$[Co(en)_2(NO_2)(ONO)]$*d*-BCS[2], *d-cis*-$[Co(en)_2(NO_2)(ONO)]ClO_4$[2] and *dl-cis*-$[Co(en)_2(NO_2)(ONO)]ClO_4$[2] had values of $\epsilon_{408\ m\mu} = 82$, $\epsilon_{434} = 106$, $\epsilon_{439} = 113$, $\epsilon_{461} = 130 \pm 2$ while the extinction coefficients for *d-cis*-$[Co(en)_2(NO_2)_2]$*d*-BCS[3], *d-cis*-$[Co(en)_2(NO_2)_2]ClO_4$ and *dl-cis*-$[Co(en)_2(NO_2)_2]ClO_4$[4] were $\epsilon_{408} = 120$, $\epsilon_{434} = 180$, $\epsilon_{439} = 181$, $\epsilon_{461} = 129 \pm 2$.

Either I or II mutarotates rapidly at room temperature reaching a constant value after several hours owing to the formation of the optically stable *d-cis*-$[Co(en)_2(N_2O)_2]^+$ ion. On warming this with dilute sodium hydroxide solution overnight, only the activity *of* the resolving agent remains. Table I compares the observed changes in rotation with those calculated. Preliminary kinetic studies indicate that the rate of mutarotation and the rate of conversion to the nitro form are equal, and have a half-time of about 70 minutes (19°). Thus the reaction

$$d\text{-}cis\text{-}[Co(en)_2(NO_2)(ONO)]^+ \longrightarrow d\text{-}cis\text{-}[Co(en)_2(NO_2)_2]^+$$

proceeds with no appreciable racemization and since the *d*-form of the starting material and the product is the least soluble diastereomer with *d*-BCS^-, the generic configuration is probably retained.[5] Tracer experiments now in progress indicate that this reaction proceeds completely by an intramolecular process.

TABLE I

MOLECULAR ROTATIONS

	Compound I		Compound II	
	Obs.	Calcd.	Obs.	Calcd.
Initial[2]	+469	+470	+228	+230
After 24 hours	+394	+384	+146	+144
After heating in dilute NaOH	+240	+241	+ 0	+ 0

In the near future a more detailed account of this work as well as new results on the kinetics of these reactions will be communicated.

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[1] M. Linhard, H. Seibert and M. Weigel, *Z. anorg. Chem.*, **278**, 287 (1955).

[2] Since the rate of reaction is much more rapid in solution, all absorption spectra and optical rotations have been extrapolated to the time of addition to water.

[3] Prepared by allowing *d-cis*-$[Co(en)_2(NO_2)(ONO)]$*d*-BCS to stand in water overnight.

[4] A. Werner, *Ber.*, **44**, 2452 (1911).

[5] A. Werner, *Bull. soc. chim.*, [4] **11**, xix (1912); J. P. Mathiew, *Compt. rend.*, **199**, 278 (1934); **201**, 1183 (1935).

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THE REQUIREMENT OF TRIPHOSPHOPYRIDINE NUCLEOTIDE IN FATTY ACID SYNTHESIS[1]

Sir:

The enzymatic reactions involved in the biological oxidation of fatty acids have been investigated extensively. It has been postulated[2] that fatty acids are synthesized from acetyl Coenzyme A (CoA) by a reversal of the oxidative pathway.

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[1] This work was supported in part by a grant from the National Heart Institute, U. S. Public Health Service.

[2] F. Lynen and S. Ochoa, *Biochim. et Biophys. Acta*, **12**, 299 (1953).