mol) and fluorosulfonic acid[13] (200 ml) were stirred overnight in 500-ml round-bottomed flask equipped with condenser and drying tube. The reaction mixture was heated to 80° and maintained at that temperature for 2 hr, cooled and poured onto cracked ice with vigorous stirring. The product was filtered, washed with water and then dissolved in methylene chloride. After drying the methylene chloride solution with $MgSO_4$ the solvent was evaporated and the product recrystallized from ether–methanol to give 12 g (48%) of product, mp >310°. At temperatures above 200° the material darkens and continues this color change to ~310°. At this temperature decomposition takes place with the evolution of bromine. Thus the melting point cannot be used as a criterion of purity. The infrared spectrum showed the antisymmetric and symmetric –S=O stretching modes at 1458 and 1259 cm^{-1}, respectively. The molecular weight by mass spectroscopy was found to be 1088 (^{79}Br). The ^{19}F nmr gave a singlet a −51.2 ppm from $CFCl_3$ in good agreement with the proposed structure.

Anal. Calcd for $C_{10}Br_{11}SO_3F$: C, 10.93; H, 0.00; Br, 80.04; S, 2.92; F, 1.73; O, 4.38. Found: C, 11.00; H, <0.30; Br, 80.00; S, 2.95; F, 1.66; 0O, 4.00.

Chlorosulfonic Acid, Undecabromopentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-yl Ester (4a).—Hexabromocyclopentadiene (50 g, 0.0925 mol) and chlorosulfonic acid (250 g) were placed in a 500-ml round-bottom flask equipped with magnetic stirrer, condenser, and drying tube. The reaction mixture was heated with vigorous stirring for 2 hr at 50°. The reaction mixture was cooled to ice bath temperature and the white precipitate that formed during the reaction and cooling process was removed by filtration through a sintered glass filter. After slurrying with carbon tetrachloride, filtering, and drying, 40 g (78%) of the crude chlorosulfate ester was obtained. Attempts to purify the crude chlorosulfate resulted in decomposition as evidenced by the disappearance of the SO_2 stretching vibrations at 1429 and 1205 cm^{-1}, respectively, in the infrared and the formation of –OH stretching bands in the 3300-cm^{-1} region.

Decabromopentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one (1b). Procedure A.—The fluorosulfate ester (3.0 g, 0.0027 mol) was dissolved in tetrahydrofuran (30 ml) and 30 ml of 0.4 *N* potassium hydroxide was added to the solution. The reaction mixture was stirred for 20 min, diluted with water (75 ml) and acidified with concentrated hydrochloric acid. The acidified solution was extracted with methylene chloride and the extract dried (Na_2SO_4) and evaporated to give a 70% yield of the crude ketone hydrate. The ketone monohydrate was obtained by the addition of hexane to a benzene acetone (2:1) solution of the crude hydrate. Purified hydrate 5 was vacuum dried at ~125° and 10 mm pressure to give the anhydrous ketone **1b**, mp >330°. The mass spectrum showed a molecular ion peak at *m/e* 926 (calcd for $C_{10}Br_{10}O$, *m/e* 926), ir (split mull) 1798 cm^{-1} (C=O).

Anal.[14] Calcd for $C_{10}Br_{10}O$: C, 12.82; H, 0.00; Br, 85.47. Found: C, 13.30; H, <0.2; Br, 85.1.

Procedure B.—The chlorosulfate ester (10 g) was dissolved in 10% aqueous acetone (10 ml). The dissolution and/or reaction of the ester resulted in a mild exothermic reaction. After cooling to room temperature, the nearly colorless solution was poured onto ice–water and the precipitate filtered and dried. Recrystallization and drying as described above gave pure anhydrous ketone.

Methyl Hemiketal of Decabromopentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one (6).—Hydrate 5 was recrystallized from anhydrous methanol containing a trace of mineral acid to give product mp >330°: ir (split mull) 2950–2850 and 1450–1435 (CH_3), 3512 cm^{-1} (OH); nmr ($CDCl_3$) δ 3.66 (s, 3, OCH_3), 2.98 (s, 1, OH). The mass spectrum showed a molecular ion peak at *m/e* 958 (calcd for $C_{11}H_4Br_{10}O_2$, *m/e* 928).

Anal. Calcd for $C_{11}H_4Br_{10}O_2$: C, 13.64; H, 0.42; Br, 82.64. Found: C, 13.80; H, 0.60; Br, 82.5.

Registry No.—**1b,** 19581-67-0; **4b,** 19581-66-9; **6,** 19613-61-7.

Acknowledgment.—The authors are grateful to Dr. J. Heeschen for the ^{19}F nmr experiment, to Mr. R. Nyquist for determining the infrared spectra, and to Dr. L. Shadoff for the mass spectral data. We are indebted to Mr. L. Swim and his associates for the elemental analyses reported herein.

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[13] CAUTION: The addition of fluorosulfonic acid to water is a violent reaction. The decomposition must be carried out in a hooded area with adequate facial protection, etc. It should also be noted that skin burns resulting from contact with fluorosulfonic acid are often reluctant to heal!

[14] All attempts to obtain acceptable analyses for **1b** or **5** were unsuccessful, presumably due to the facile hydration and dehydration reactions.

A Calculation of the Optical Activity of a Trefoil Knot

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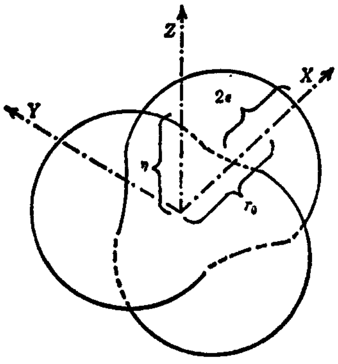
The optical activity of a trefoil, a ring which contains a simple overhand knot, is a property of the structure which distinguishes it from the unknotted ring.[3] To obtain some feeling for the magnitude and sign of rotation expected we have carried out a straightforward Kirkwood calculation[4] of the activity expected for a polymethylene trefoil $(CH_2)_m$.

A particular conformation of the knot of absolute configuration I may be represented by the parametric equations[5]



I

$$r = r_0 + \epsilon \cos\left(\frac{3}{2}\theta\right)$$

$$z = \eta \sin\left(\frac{3}{2}\theta\right) \qquad (1)$$

with

$$0 \leq \theta \leq 4\pi, \quad 0 < |\epsilon| < r_0, \quad \eta > 0$$

The chain was divided into n segments (n = 10, 25, or 50) and the fragments were treated as the individually polarizable groups characteristic of the Kirkwood

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[4] J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937). Note correction in sign in W. W. Wood, W. Fickett, and J. G. Kirkwood, *ibid.*, **20**, 561 (1952), footnote 2.

[5] We wish to thank Dr. F. H. Stillinger for a discussion on this point.

theory. The positions of these fragments were taken as those of the center of the segments and their orientations as those of the tangents to the curve at the center. With these values the sum[4] given in eq 2 was evaluated,

$$\Sigma_G = \frac{1}{6}\sum_{i,k=1}^{n}\frac{1}{R_{ik}^3}\left[\vec{b_i}\cdot\vec{b_k} - \frac{3(\vec{b_i}\cdot\vec{R_{ik}})\,(\vec{b_k}\cdot\vec{R_{ik}})}{R_{ik}^2}\right] \times \vec{R_{ik}}\cdot(\vec{b_i} \times \vec{b_k}) \qquad (2)$$

where b_i is the direction of the unit vector at the center of the ith segment and R_{ik} is the distance between the center of the ith and kth segments. Taking the isotropic and anisotropic polarizability, α and β, of an equivalent length of a linear polymethylene chain[6] as characteristic of those of each of the segments, we then obtain the Kirkwood rotation as[4]

$$[\alpha]_D = 4.96 \times 10^5\left(\frac{n^2+2}{3M}\right) \times \alpha^2\beta^2\Sigma_G \qquad (3)$$

where n is the refractive index of the medium and M the molecular weight.

The values of the rotation are largely independent of the number of segments assumed, and we find for m = 66 a rotation $[\alpha]_D$ +2.1 for r_0 = 5.7 Å, ϵ = 2.09 Å, and η = 2.7 Å. While smaller knots are possible, steric interactions prevent the particular atomic arrangement given by eq 1. The small value of $[\alpha]_D$ may be viewed as caused, in part, by the fact that some portions of I are right-handed helices and others are left-handed helices. Extensive cancellation thus results.

The small value arising from the cancellation reduces our confidence in the assignment of absolute configuration. Small deviations of the structure from that of eq 1, by straightening one portion of a curve or by rotating a portion by 90° about its chord, can lead to increases in α by factors of 10 or to decreases and changes in sign. The rotation is likely to be a sensitive function of the environment of the molecule for all but the smallest and tightest knots near C_{50}. Near the lower limit the deviations from eq 1 are sufficiently large that the calculation is of doubtful validity.

[6] C. W. Bann and R. de P. Daubeny, *Trans. Faraday Soc.*, **50**, 1173 (1954).

The Preparation and Redistribution of 4-(2,6-Diphenylphenoxy)-2,6-diphenylphenol

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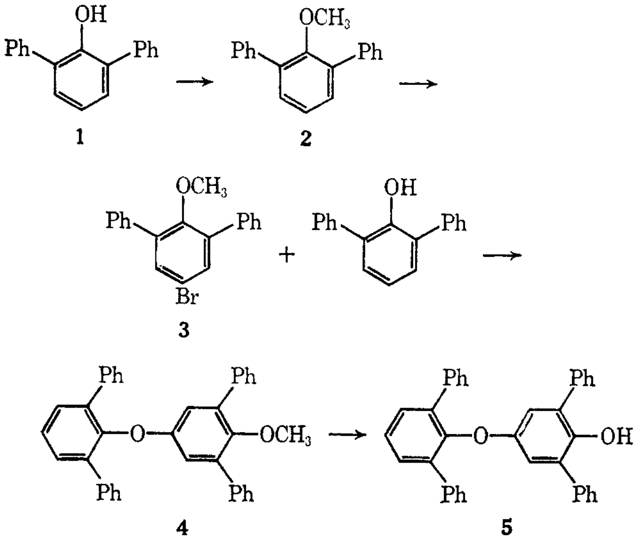
The discovery by Hay[1] that 2,6-diphenylphenol could be oxidatively coupled to form poly(2,6-diphenylphenylene oxide) led into a closer examination of the chemistry of 2,6-diphenylphenol. This molecule appears to be relatively hindered and the relative ease of its oxidative coupling was interesting. The backbone structure of poly(2,6-diphenylphenylene oxide) is identical with that of poly(2,6-dimethylphenylene oxide)[2] and this work was undertaken to see whether other reactions of 2,6-diphenyl-substituted phenols were similar to 2,6-dimethylphenol.

The phenyl-substituted analog of 2,6-xylenol dimer[3] was prepared. This is 4-(2,6-diphenylphenoxy)-2,6-diphenylphenol (5) and was prepared by the following sequence of reactions. The phenol **1** was converted to the methyl ether **2** which was brominated to give 4-bromo-2,6-diphenylanisole **3**. This was coupled with 2,6-diphenylphenol in an Ullmann reaction to give 4-(2,6-diphenylphenoxy)-2,6-diphenylanisole (**4**) which was cleaved to give the phenol dimer **5**.



When the dimer **5** was dissolved in benzene and treated with a radical source such as tri-*t*-butylphenoxyl it underwent redistribution.[3,4] The solution was silylated[5] with bis(trimethylsilyl)acetamide and examined by thin layer chromatography (tlc) or vapor phase chromatography (vpc). The vpc showed three components which were identified as monomer **1**, dimer **5**, and, by analogy, trimer **6**. These materials arise from a redistribution of the dimer radical **5a**.

The same solution was examined on tlc and showed a spectrum of 11 spots in decreasing amounts. The first two were identified as monomer **1** and dimer **5**. The other spots were assigned as being the higher oligomers of 2,6-diphenylphenol. This was further substantiated by degrading a sample of 2,6-diphenylphenol polymer with 2,6-diphenylphenol according to the method of Cooper, Gilbert, and Finkbeiner.[4] The resulting mixture gave the same series of compounds on tlc.

The final proof that the reactions of 2,6-diphenylphenol dimer **5** are identical with those of the 2,6-dimethylphenol dimer is that **5** can be polymerized to poly(2,6-diphenylphenylene oxide) by the use of metal oxides such as lead dioxide.[6] The polymer obtained from this oxidation is identical with polymer obtained from the copper–amine-catalyzed polymerization of 2,6-diphenylphenol.

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[1] A. S. Hay, unpublished work.

[2] A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Amer. Chem. Soc.*, **81**, 6335 (1959).

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[4] G. D. Cooper, A. R. Gilbert, and H. Finkbeiner, Polymer Preprints, Winter Meeting of the American Chemical Society, Phoenix, Ariz., 1966, p 166.

[5] J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Amer. Chem. Soc.*, **88**, 3390 (1966).

[6] H.-D. Becker, U. S. Patent 3,390,425 (1968).