with saturated aqueous oxalic acid. The aqueous solution was extracted to give 184 mg of crude oily product, which was passed in ether through a short column of Florisil. Sublimation at 65–70° (0.01 mm) and recrystallizations from pentane yielded 99 mg (26%) of white crystals: mp 54–55°; ir 1610, 1580, 1350, 925 cm^{-1}, no C=O absorption; uv 219 nm (ϵ 6960), 228 (7550), 282 (2720), 288 s (2360); nmr δ 0.85 (3 H s), 1.1–2.85 (9 H complex), 3.75 (3 H s), 3.9 (4 H m), 6.5–7.1 (3 H complex).

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.41; H, 8.16.

***cis*-9a-Methyl Compound.**—Potassium amide was prepared by addition of 39 mg (1.0 mg-atom) of K to 15 ml of anhydrous NH_3 containing *ca.* 1 mg of $FeCl_3$ in a flask equipped with a Dry Ice condenser. The suspension was stirred for 30 min, during which time the color changed from blue to gray-black; to this was added a solution of 50 mg of *trans*-methyl compound (0.183 mmol) in 5 ml of dry THF. The mixture was refluxed for 4 hr and worked up by addition of excess solid NH_4Cl. The usual work-up provided 48 mg of crude oily product, which was chromatographed. Appropriately combined fractions were sublimed at 90° (0.01 mm) and recrystallized from pentane to give 25 mg (50%) of white needles; mp 93–94°; ir 1610, 1585, 1355 m, 925 cm^{-1}, no C=O absorption; uv 220 s nm (ϵ 7570), 228 (7850), 282 (2780), 228 s (2440); nmr δ 1.1–2.9 (9 H complex), 1.25 (3 H s), 3.7 (3 H s), 3.8 (4 H m), 6.45–6.65 (2 H m), 6.9 (1 H d, J = 8.5 Hz).

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.34; H, 8.17.

***p*-Toluenesulfonate Ester of Unsaturated Alcohol 4u.**—To a cold solution of unsaturated alcohol **4u** (1.0 g, 3.47 mmol) in dry pyridine (10 ml) was added *p*-toluenesulfonyl chloride (820 mg, 4.31 mmol) and the flask was flushed with N_2 and stoppered; the mixture was stirred for 4–5 hr at 0° and then at room temperature for 24 hr. The mixture was recooled to 0° and neutralized with dilute aqueous HCl. Extraction of the diluted mixture provided material which was crystallized from ether to give 563 mg (37%) of tan solid, mp 109–112°, ir 1350 cm^{-1}, no OH absorption in the 3600–3200 cm^{-1} region.

The *p*-toluenesulfonate ester of cis alcohol 4c and its preparation have been described previously.[4]

Methanesulfonate Ester of Cis Alcohol 4c.—To a stirred, ice-cold solution of cis alcohol **4c** (1.5 g, 5.28 mmol) in dry pyridine (10 ml) was added freshly distilled methanesulfonyl chloride (0.63 ml, 7.0 mmol) and the flask was flushed with N_2 and stoppered; the solution was stirred for 4–5 hr in an ice bath at 0° and then at room temperature for 32 hr. The mixture was recooled to 0° and neutralized with dilute aqueous HCl. Extraction of the diluted solution gave a viscous yellow oil, which failed to crystallize from a variety of solvents: ir 1370, 1350 cm^{-1}, no OH absorption in the 3600–3200 cm^{-1} region.

Registry No.—**4c** (methanesulfonate), 33885-17-5; **4u** (tosylate), 33885-18-6; **5c**, 13673-64-8; **5t**, 33885-20-0; **5u**, 33885-21-1; **6c**, 33885-22-2; **6t**, 33885-23-3; **6u**, 33885-24-4; **7t**, 33872-69-4; *cis*-9a-methyl compound, 33885-25-5; *trans*-9a-methyl compound, 33885-26-6; **10c**, 33885-27-7; **10t**, 33885-25-8; **10u**, 33885-29-9; **11c**, 33885-30-2; **11t**, 33885-31-3; **11u**, 33885-32-4; **12c**, 33885-33-5; **12t**, 33885-34-6; **12u**, 33885-35-7.

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The Resolution and Absolute Configuration of 7-Methylhexahelicene

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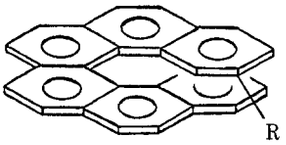
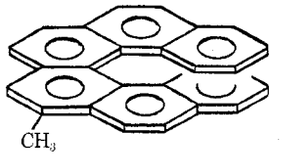
rac-7-Methylhexahelicene (**3**) is brominated to the bromomethyl derivative **4** which on treatment with trimethylphosphine is converted into the racemic quaternary phosphonium bromide **5**. By salt formation with silver D(−)-hydrogendibenzoyltartrate and recrystallization of same, a pure diastereoisomeric salt (−)-**6**$^+$·D(−)-HDBT$^-$ is isolated and converted into (−)-**5** by treatment with tetraethylammonium bromide. Aqueous alkaline treatment of (−)-**6**$^+$·D(−)-HDBT$^-$ affords (−)-**3**. All steps proceed in high yield. The above reactions provide a new method of resolution for methyl derivatives of dissymetric aromatic hydrocarbons.

When the work herein reported was started the absolute configuration of hexahelicene (**1**)[2] had not been



1, R = H
2, R = Br



(−)-3

established. Recently, the assignment of the left-handed helix (−)-**1**, as shown in the formula, has been established by X-ray analysis of (−)-2-bromohexahelicene (**2**).[3]

Because of the difficulty experienced in resolution of hexahelicene[2,4] by the use of α-(2,4,5,7-tetranitro-9-fluorenylidenaminooxy)propionic acid (TAPA),[5] a new method for the resolution of a helicene was sought which would involve a compound whose absolute configuration could be established by X-ray crystallographic methods. This method has been discovered and is described herein. However, since the problem of the helicenes has been solved[3] the X-ray work has not been carried out. Our method is outlined in Chart I.[6]

Bromination of 7-methylhexahelicene (**3**)[7] to 7-

(1) Postdoctoral fellow supported by Grant G12445X of the National Science Foundation.

(2) M. S. Newman and D. Lednicer, *J. Amer. Chem. Soc.*, **78**, 4765 (1956).

(3) D. A. Lightner, D. T. Hefelfinger, G. W. Frank, T. W. Powers, and K. N. Trueblood, *Nature (London)*, **232**, 124 (1971). Further literature references to other related work are given in this paper.

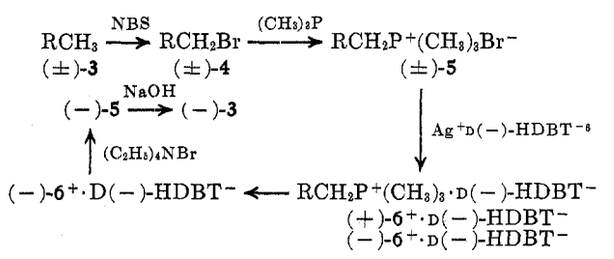
(4) M. S. Newman, R. S. Darlak, and L. Tsai, *J. Amer. Chem. Soc.*, **89**, 6191 (1967).

(5) M. S. Newman and W. B. Lutz, *ibid.*, **78**, 2469 (1956).

(6) Ag$^+$D(−)-HDBT$^-$ is silver D(−)-hydrogendibenzoyltartrate, a compound first used for resolution of an asymmetric tetracovalent phosphorus compound by D. M. Coyne, W. E. McEwen, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **78**, 3061 (1956). Both the D(−)- and L(+)-dibenzoyltartaric acids can be obtained from the Norse Laboratories, Inc., Santa Barbara, Calif. 93103.

(7) 7-Methylhexahelicene was first prepared here (unpublished work) by Dr. David J. Collins in 1959.

CHART I



hexahelicylmethyl bromide (**4**)[8] was accomplished in good yield with *N*-bromosuccinimide. Treatment of **4** with trimethylphosphine afforded the beautifully crystalline phosphonium salt **5** in almost quantitative yield. On reaction of **5** with silver D(−)-hydrogendibenzoyltartrate in methanol a high yield of a mixture of diastereoisomeric D(−)-HDBT salts (**6**) was obtained. On one crystallization from ethanol–1-propanol about 50% of the theoretical amount of the (−)**6**$^+$·D(−)-HDBT$^-$ isomer separated. Further recrystallization did not appreciably improve the specific rotation. On refluxing (−)-**6**$^+$·D(−)-HDBT$^-$ in methanol with tetraethylammonium bromide conversion to (−)-**5** was obtained in over 90% yield. This salt was readily crystallized from methanol–ether to yield crystals which seemed suitable for X-ray studies. Finally, on treatment of (−)-**5** with aqueous sodium hydroxide at room temperature (−)-**3** was obtained in high yield.[9] We assume that (−)-**3** and (−)-**5** exist as left-handed helices, as established for (−)-**1**, because of the similarity of the negative Cotton effect observed in the regions examined.[3]

This method of resolution is of special interest because a quaternary phosphonium compound **5**, in which the dissymmetry is not centered on phosphorus, has successfully been resolved. In addition, the ease of crystallization and separation of the diastereoisomeric phosphonium salts makes the resolution relatively simple.

Experimental Section[10]

(±)-**7-Methylhexahelicene** (**3**).[7]—A Grignard reagent was prepared by treating 1.67 g of magnesium in 50 ml of ether with 9.8 g of methyl iodide. After all of the magnesium had reacted, 300 ml of benzene was added and the ether was largely removed by distillation. To this reagent was added a solution of 20 g of 7,8,8a,9,10,16c-hexahydro-7-oxohexahelicene[4] in 500 ml of benzene. After being refluxed for 26 hr the mixture was worked up as usual. Chromatography over silica gel in benzene yielded 14.0 g of a first fraction from which a light yellow solid, presumably the expected olefin, mp 192–197°, could be crystallized. In addition, a second fraction from which 2.0 g of starting ketone could be crystallized and 1.4 g of a third fraction, presumably the tertiary alcohol, were obtained. The crude olefin (9.2 g) was aromatized as described[4] for the preparation of hexahelicene to yield 3.87 g (42%) of (±)-**3**, mp 192–194°. By chromatography and recrystallization from benzene–Skellysolve F, acetone, and benzene there was obtained the analytical sample, mp 198.0–198.5°. For further work, material of mp 192–194° was used.

Anal. Calcd for $C_{27}H_{18}$: C, 94.6; H, 5.2. Found: C, 94.7; H, 5.3.

(±)-**7-Hexahelicylmethyl Bromide** (**4**).[8]—A solution of 0.613 g of *N*-bromosuccinimide and 1.00 g of **3** in 10 ml of carbon tetrachloride was refluxed for 12 hr after the addition of a few crystals of benzoyl peroxide. On cooling the succinimide was removed by filtration and the filtrate was evaporated to dryness. Recrystallization of the residue from benzene–Skellysolve B yielded 0.99 g (78%) of **4**, mp 207–210°, suitable for further work. The analytical sample, mp 213–215°, was obtained by further recrystallization from the same solvent.

Anal. Calcd for $C_{27}H_{17}Br$: C, 77.1; H, 4.1; Br, 19.0. Found: C, 77.2; H, 4.2; Br, 19.1.

In a larger run (2.38 g of **3**) the yield of **4** was 70%.

(±)-**7-Hexahelicylmethyltrimethylphosphonium Bromide** (**5**).—To a solution of 1.00 g of **4** in 20 ml of ether and 20 ml of benzene in a three-necked flask under nitrogen equipped with a Dry Ice cooled condenser, septa, and magnetic stirrer was added about 1.5 ml of Dry Ice cooled trimethylphosphine (caution, toxicity) from a syringe. Solid **5** precipitated immediately. The mixture was stirred overnight (with water condenser instead of Dry Ice condenser) and then heated to reflux for 4 hr. The yellow solid was collected by filtration and the cooled mixture was washed with dry benzene. After drying *in vacuo* the solid was dissolved in 100 ml of hot methanol and the solution was concentrated to *ca.* 30 ml. On cooling 1.105 g (93%) of **5**, mp *ca.* 350° dec after darkening at 335°, nmr [CD_3OD–$(CD_3)_2SO$, 1:1] δ (TMS) 2.0 [9 H, d, J = 14.5 Hz, $P(CH_3)_3$], 4.59 (2 H, d, J = 17.5 Hz, $-CH_2P$), 6.3–8.8 (15 H, m, ArH), was obtained suitable for further use.

Anal. Calcd for $C_{30}H_{26}BrP$: C, 72.4; H, 5.2; Br, 16.1; P, 6.2. Found: C, 72.3; H, 5.3; Br, 15.9; P, 6.0.

The phosphonium bromide **5** slowly absorbs moisture on standing. As a result, marked solubility differences were observed during the recrystallization process. The presence of moisture, as revealed by the strong O–H stretching absorption in the ir spectrum, was gradually removed by heating.

(−)-**7-Hexahelicylmethyltrimethylphosphonium D(−)-Hydrogendibenzoyltartrate** [(−)-**6**$^+$·D(−)-**HDBT**$^-$)].—To a solution at room temperature (previously warmed to effect solution) of 1.004 g of **5** in 50 ml of methanol was added 0.951 g of silver D(−)-hydrogendibenzoyltartrate prepared[6] from D(−)-dibenzoyltartaric acid, $[\alpha]^{27}D$ −111°. The heterogeneous mixture was magnetically stirred at ambient temperature for 17 hr in the dark. After addition of 15 ml of methanol the yellow suspension was heated to reflux for 72 hr. The silver bromide (89%) was collected by filtration and washed well with methanol. The filtrate was evaporated to dryness and the residue was stirred for 1 hr with 125 ml of distilled water. The solid was collected, washed with water, and dried *in vacuo* over P_2O_5 to yield 1.353 g (87%) of (±)-**6**$^+$·D(−)-HDBT$^-$: mp 158–159° dec; ir 3500 (OH), 1730 cm^{-1} (s) (C=O); nmr (CD_3OD) δ (TMS) 1.85 [9 H, d, J = 14.5 Hz, $P(CH_3)_3$], 4.37 (2 H, d, J = 16 Hz, $-CH_2P$), 6.05 (2 H, s, methine H of HDBT), 6.3–8.4 [25 H, m, (Ar H, C_6H_5)]. The acidic proton was not observed because of exchange with the deuterated solvent. Recrystallization of the crude salt from 70 ml of ethanol–1-propanol (1:1) yielded 402 mg of (−)-**6**$^+$·D(−)-HDBT$^-$ as yellow crystals, mp 157.5–158.5° dec, after 12 hr. The specific rotations were obtained at the wavelengths indicated[10] from 0.574 mg of salt in 2 ml of absolute methanol: −1105° (589 mμ), −1181° (578), −1457° (546), −4231° (436), and 0° (365). After two further recrystallizations from ethanol, 136 mg of (−)-**6**$^+$·D(−)-HDBT$^-$ was obtained which gave the following specific rotations from a solution of 0.128 mg in 2 ml of methanol: −1109° (589), −1297° (578), −1625° (546), −4672° (436), and 0° (365). Hence we believe that almost completely resolved material was obtained in the first crystallization. The crystals from the first crop evidently retained one molecule each of ethanol and 1-propanol as

(8) The bromination of **3** was done here by Dr. R. A. Darlak in 1965.

(9) For analogous reactions, see A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, New York, N. Y., 1967, p 254.

(10) Melting points are uncorrected and were determined on a Thomas-Hoover capillary melting point apparatus. A melting point block was used for those above 280°. Infrared were obtained on a Perkin-Elmer Infracord Model 137 spectrophotometer in KBr pellets. Nuclear magnetic resonance spectra were determined on a Varian 60 high-resolution spectrometer using TMS as an internal standard. The mass spectra were determined by use of the direct inlet system on an AEI MS-902 double-focusing mass spectrometer. Optical rotations were measured on a Perkin-Elmer Model 141 Polarimeter (accurate to 0.001°) using a 10-cm Micro-cell with inner glass tube diameter of 3.4 mm and a cell volume of 1 ml. In a typical rotation determination, the sample was weighed on a Cahn Electro-Balance (accurate to 0.001 mg), dissolved in a suitable solvent in a 2-ml Kimax volumetric flask, and 1 ml of the prepared solution of known concentration was transferred into the Micro-cell for immediate measuring in the instrument. Measuring accuracy with micro cells is claimed to be approximately ±0.2% for rotations >1° by the manufacturer. Elemental microanalyses were determined by Galbraith Laboratories, Knoxville, Tenn.

judged by the analysis. Such inclusion of solvent is not uncommon with phosphonium salts.[11]

Anal. Calcd for $C_{48}H_{39}O_3P \cdot C_2H_6O \cdot C_3H_8O$: C, 72.5; H, 6.0; P, 3.5. Found: C, 72.5; H, 5.7; P, 3.4.

(−)-7-Hexahelicylmethyltrimethylphosphonium Bromide (5).—A solution of 120 mg of (−)-6$^+$·D(−)-HDBT$^-$ ([α]^{23}D −1109°) and 3.5 g of tetraethylammonium bromide in 18 ml of methanol was refluxed for 48 hr and allowed to stir at room temperature for 72 hr. The methanol was removed under reduced pressure and the residue was stirred with 40 ml of water for 12 hr. The solid was collected by filtration, washed with water, and dried *in vacuo* over P_2O_5. Crystallization from methanol afforded 72.9 mg (95%) of (−)-**5**, mp *ca.* 354° dec. The infrared spectrum was identical with that of (±)-**5**. The following specific rotations were obtained at 23° from a solution of 0.400 mg in 2 ml of methanol: −1930° (589 mμ), −2070° (578), −2559° (546), −7563° (436), and 0° (365). Further recrystallization from methanol did not change the rotation significantly.

(−)-7-Methylhexahelicene (3).—A solution of 20 mg of (−)-**5** ([α]^{23}D −1881°) was stirred with 5 ml of 10% sodium hydroxide at ambient temperature for 24 hr. The yellow solid was collected by filtration and washed well with water. After drying *in vacuo* over P_2O_5, there was obtained 12.6 mg (92%) of (−)-**3**, mp 175–180°. One recrystallization from 2-propanol yielded 10.5 mg of (−)-**3**, mp 185–186°, with the following specific rotations (from 0.356 mg in 2 ml of chloroform): −3157° (589 mμ), −3399° (578), −4185° (546), −12,332° (436), and +219° (365). The structure of (−)-**3** was established by comparison with that of (±)-**3** with respect to ir and mass spectrum (M$^+$, 342).

Registry No.—(±)-**3**, 33835-50-6; (−)-**3**, 33835-51-7; (±)-**4**, 33872-33-2; (±)-**5**, 33835-52-8; (−)-**5**, 33835-53-9; (±)-6$^+$·D(−)-HDBT$^-$, 33835-54-0; (−)-6$^+$·D(−)-HDBT$^-$, 33835-55-1.

(11) M. Davis and F. G. Mann, *J. Chem. Soc.*, 3770 (1964); C. H. Chen and K. D. Berlin, *J. Org. Chem.*, **36**, 2791 (1971).

The Conformations of Electronegatively Substituted Imines

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Contribution No. 1870 from the Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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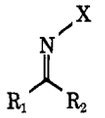
The preferred conformations of 1,1,1-trifluoroacetone hydrazone and azine have the substituent anti to the trifluoromethyl group. The assignments are based on the stereospecificity of six-bond, proton–fluorine coupling in selected *N,N*-dimethyl derivatives and correlations of the fluorine chemical shifts of syn and anti trifluoromethyl groups in hexafluoroacetone imine derivatives. Allylic proton–fluorine coupling is not a reliable indicator of stereochemistry.

The preferred conformations of unsymmetrical imines, hydrazones, oximes, azines, etc., are of continuing interest.[1] A related problem in symmetrical derivatives is the correct spectral identification of the syn and anti groups.[2] For those classes of compounds **1** where R_1 and R_2 are hydrocarbon, steric arguments suffice to predict conformation.[1,3,4]

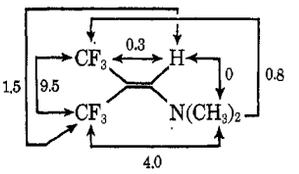


1, X = H, CH_3, NH_2, OH, F...
1a, $R_1 = CF_3$, $R_2 = CH_3$, X = NH_2

Trifluoroacetone hydrazone[5] (**1a**) and trifluoroacetone azine have single conformations in solution. Although steric arguments predict that the trifluoromethyl and the substituent should be anti,[6] dipole interactions between electronegative substituents may stabilize the syn form.[7] The purpose of this study is to determine the conformation of trifluoroacetone imine derivatives.

Results.—No single, simple, physical measurement unambiguously identifies the conformations of trifluoroacetone imines. Therefore a series of indirect studies was performed.

Six-Bond, Proton–Fluorine Coupling.—The methyl protons of enamine **2**[8] couple differently to the cis and trans trifluoromethyl groups. A 1.8-Hz, six-bond, proton–fluorine coupling was observed in the *trans*-hexafluorobutyne–dimethylamine adduct **3**, but the coupling in the cis isomer was not mentioned.[9] Couplings between all pairs of nuclei in both *cis*- and *trans*-**3** have now been observed and include the 0.6-Hz, six-bond, proton–fluorine coupling in *cis*-**3**. Hexa-



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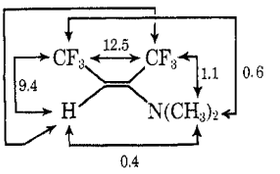
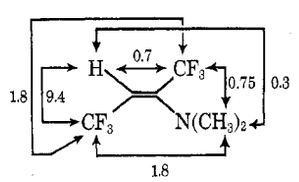
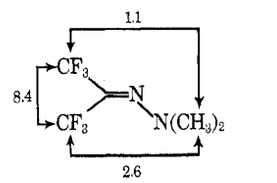


cis-**3**



trans-**3**



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(1) G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Amer. Chem. Soc.*, **84**, 753 (1962); G. J. Karabatsos, F. M. Vane, R. A. Taller, and N. Hsi, *ibid.*, **86**, 3351 (1964).

(2) For the use of the new Eu chelates to identify oxime conformations see Z. W. Wolkowski, *Tetrahedron Lett.*, 825 (1971); K. D. Berlin and S. Rengaraju, *J. Org. Chem.*, **36**, 2912 (1971).

(3) E. Arnal, J. Elguero, R. Jacquier, C. Marzin, and J. Wylde, *Bull. Chem. Soc. Fr.*, 877 (1965); J. Elguero, R. Jacquier, and C. Marzin, *ibid.*, 713 (1968).

(4) Yu. P. Kitaev, B. I. Buzykin, and T. V. Troepol'skaya, *Russ. Chem. Rev.*, 441 (1970).

(5) R. A. Sheppard and P. L. Sciaraffa, *J. Org. Chem.*, **31**, 964 (1966).

(6) R. Filler in "Advances in Fluorine Chemistry," Vol. 6, J. C. Tatlow, R. D. Peacock, and H. H. Hyman, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1970.

(7) H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960); R. E. Wood and D. P. Stevenson, *J. Amer. Chem. Soc.*, **63**, 1650 (1941).

(8) Yu. A. Cheburkov, N. Mukhamadaliev, Yu. E. Aronov, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1478 (1965).

(9) W. R. Cullen, D. S. Dawson, and G. E. Styan, *Can. J. Chem.*, **43**, 3392 (1965).