**1-(1-Cyclohexenyl)propene**[14] was obtained from **11**. The major and minor isomers were identical with the authentic samples of the *E* and *Z* isomers, respectively.[24]

**1-(1-Cyclohexenyl)butene**[14] was obtained from **12**. The vinyl region of the NMR spectrum was very similar to that of the *E* isomer obtained from **11** and on that basis was assigned the same configuration: NMR $\delta$ 6.11–5.20 (m, 3, which contained the low-field half of an AB quartet, $J_{AB}$ = 15 Hz), 2.34–1.33 (m, 10), 1.00 (t, 3, $J$ = 6.5 Hz).

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**Registry No.**—**1a**, 54354-14-2; **1b**, 53101-85-2; **1c**, 40789-98-8; **1d**, 17042-24-9; **1e**, 42904-05-2; **2a**, 7301-94-2; **2b**, 54354-15-3; **2c**, 54354-16-4; *cis*-**3**, 33765-35-4; *trans*-**3**, 33765-34-3; *cis*-**4**, 54354-17-5; *trans*-**4**, 54354-18-6; *cis*-**5**, 54354-19-7; *trans*-**5**, 54354-20-0; *cis*-**6**, 54354-21-1; *trans*-**6**, 54354-22-2; *cis*-**7**, 54354-23-3; *trans*-**7**, 54354-24-4; *cis*-**8**, 54354-25-5; *trans*-**8**, 54354-26-6; *cis*-**9**, 54354-27-7; *trans*-**9**, 54354-28-8; *cis*-**10**, 54354-29-9; *trans*-**10**, 54354-30-2; *cis*-**11**, 54354-31-3; *trans*-**11**, 54354-32-4; *cis*-**12**, 54354-33-5; *trans*-**12**, 54354-34-6; 2-bromo-3-pentanone, 815-52-1; 3-pentanone, 96-22-0; 2-bromopropanal, 19967-57-8; 3-methyl-2-buten-1-yltriphenylphosphonium bromide, 1530-34-3; triphenylphosphine hydrobromide, 6399-81-1; isoprene, 78-79-5; (*Z*)-1-(1-cyclohexenyl)propene, 5680-41-1; (*E*)-1-(1-cyclohexenyl)propene, 54354-35-7; ethyltriphenylphosphonium bromide, 1530-32-1; cyclohexenecarboxaldehyde, 30326-86-4; (*E,Z*)-2,4-hexadiene, 5194-50-3; (*E,E*)-2,4-hexadiene, 5194-51-4; (2*E*,4*Z*)-heptadiene, 54354-36-8; (*E,E*)-2,4-heptadiene, 2384-94-3; 2-methyl-(3*E*,5*E*)-octadiene, 54354-37-9; 2-methyl-(3*E*,5*Z*)-octadiene, 54354-38-0; 3-methyl-(2*E*,4*E*)-hexadiene, 54354-39-1; 3-methyl-(2*Z*,4*E*)-hexadiene, 54354-40-4; 3-methyl-(2*E*,4*E*)-heptadiene, 54354-41-5; 3-methyl-(2*Z*,4*E*)-heptadiene, 54354-42-6; 3-ethyl-(2*E*,4*E*)-hexadiene, 54354-43-7; 3-ethyl-(2*Z*,4*E*)-hexadiene, 54354-44-8; 3-ethyl-2,4-heptadiene, 54354-45-9; 3-ethyl-6-methyl-(2*E*,4*E*)-heptadiene, 54354-46-0; 3-ethyl-6-methyl-(2*Z*,4*E*)-heptadiene, 54354-47-1.

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# Stable Rotamers of 9,9′:9′,9″-Terfluorenyls at Room Temperature[1]

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The reactions and spatial structures for the stereoisomers $C_{39}H_{26}$, mp 293° dec (A) and mp 257° dec (B), which are stable at room temperature in solution were investigated. It is proposed from NMR spectra that these are conformational isomers, namely *s-cis,s-cis-* and *s-cis,s-trans*-9,9′:9′,9″-terfluorenyls occurring as the result of restricted rotation about the $sp^3$–$sp^3$ carbon–carbon single bonds. A isomerized to B by treatment with Raney nickel. Rotamers A and B were obtained simultaneously by the Michael addition of fluorene to 9,9′-bifluorenylidene.

During investigation on the self-condensation of fluorene (**1**) by treating with various bases, we have obtained 9,9′:9′,9″-terfluorenyl, mp 257° dec (B),[2] by reaction of **1** with sodamide. Pinck and Hilbert also obtained this compound but with mp 293° dec (A)[3] by the Michael addition of **1** to 9,9′-bifluorenylidene (**2**) (Scheme I).

A was isomerized to B, followed by thermolysis of the resulting B to give 9,9′-bifluorenyl (**3**) and **2**,[2] as established by ESR.[4] Isomers A and B were isolated simultaneously by reaction of 9-bromofluorene with methanolic potassium hydroxide in acetone or from other reactions.[5] Both compounds are stable at room temperature in solution, and give fluorenone by oxidation and **1** by reduction.[2,6] Previously we suggested that A and B could be rotational isomers around the $C_9$–$C_{9'}$–$C_{9''}$ carbon–carbon single bonds.[7]

In the preliminary communication,[8] we reported the conformations and conformational isomerizations of A and B. The present investigation gives further details on the spectral basis of the previous assignments, and is concerned with the Michael addition of **1** to **2**.

**Conformations of 9,9′:9′,9″-Terfluorenyl Isomers.** Mass spectra of A and B are virtually identical: the parent peak appears at *m/e* 494; the base peak at *m/e* 329 (9,9′-bifluorenyl cation) and *m/e* 165 (9-fluorenyl cation) are fragments whose origin can be interpreted by simple cleavage of $C_{9-9'}$ or $C_{9'-9''}$ bonds from the parent ion.

The ir spectra show absorption bands due to the methine hydrogen C–H stretching frequencies at 2899 cm$^{-1}$ for **3** (9-CH, 9′-CH) and 2917 cm$^{-1}$ for A (9-CH, 9″-CH), whereas two bands at 2883 and 2918 cm$^{-1}$ are observed for B (9-

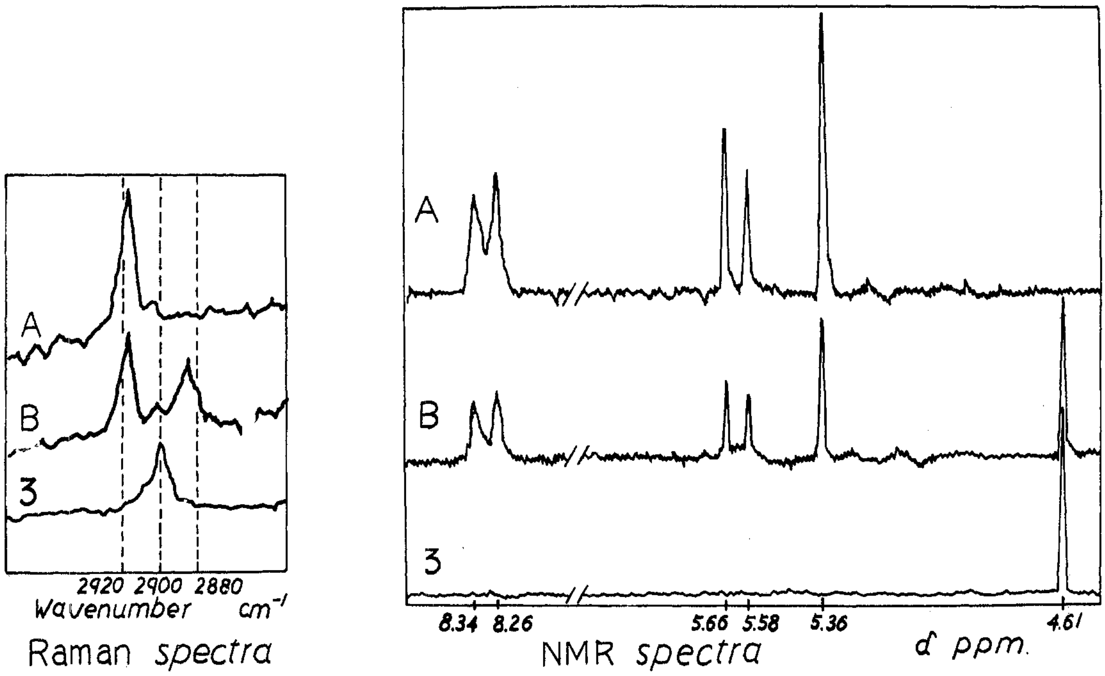
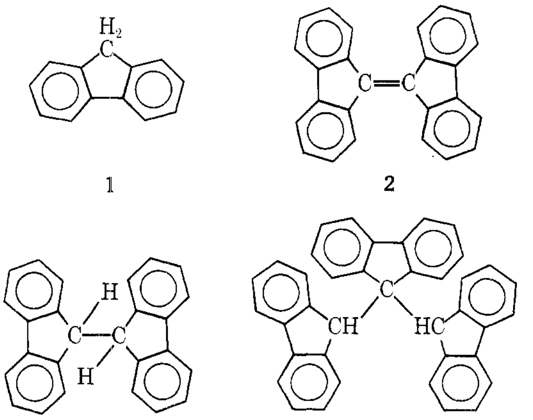


**Figure 1.** Partial Raman and NMR spectra of A, B, and 3.

**Scheme I**

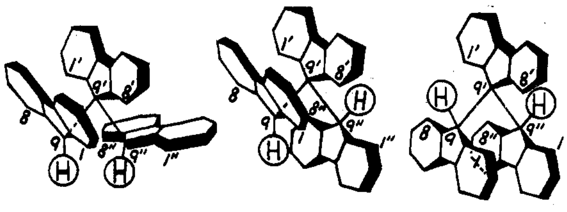


CH, 9″-CH). Similarly, there are fairly strong absorptions in the Raman spectra at 2900 cm$^{-1}$ for **3**, at 2918 cm$^{-1}$ for A, and at 2884 and 2919 cm$^{-1}$ for B, as Figure 1 shows. Therefore, the two methine frequencies in B would seem due to different conformational effects.

The NMR spectrum of **3** exhibits a 16-proton signal at 7.58–6.85 ppm (aromatic region) and a two-proton singlet from the 9- and 9′-methines at 4.61 ppm. Both A and B show a 24-proton signal at 8.34–5.58 ppm (aromatic region), a two-proton singlet of $C_9$ and $C_{9''}$ at 5.36 ppm in A, and the nonequivalent two protons at 4.61 and 5.36 ppm in B. The assignment of signals to these methine protons in **3**, A, and B was confirmed by the syntheses of the corresponding deuterated compounds.

In addition, some characteristic shifts in the NMR spectra appear at higher (5.58 and 5.66 ppm, $J = 8$ Hz) and lower (8.26 and 8.34 ppm) fields than would be expected as two doublets in both A and B; the extent of each doublet area is equivalent to two protons in A and one proton in B. Furthermore, signal intensities decreased in the NMR spectra of A-*1-d* (or 1-deuterio-9,9′:9′,9″-terfluorenyl, mp 293°C dec) and B-*1-d*.

An examination of the space-filling molecular models of 9,9′:9′,9″-terfluorenyls indicates that the rotation about the



s-trans,s-trans s-cis,s-trans (B) s-cis,s-cis (A)

**Figure 2.**

sp$^3$–sp$^3$ single bonds of $C_{9-9'}$ and $C_{9'-9''}$ is sufficiently restricted due to the close proximity of the hydrogen atoms at the 1, 8, 1′, 8′, 1″, 8″, 9, and 9″ positions, so the following three rotamers can exist in the ground state (see Figure 2).

(a) Three planes in the 9,9′:9′,9″-terfluorenyl, that is, 9- and 9″-fluorenyls and 9′-fluorenylidene, can be folded cis with respect to one another, so the molecule exists in the s-cis,s-cis conformation.

(b) Both the 9-fluorenyl and 9′-fluorenylidene planes may be folded cis with respect to each other, and that of 9″-fluorenyl may be oriented s-trans to those of the central 9′-fluorenylidene, leading to the s-cis,s-trans conformation.

(c) The 9- and 9″-fluorenyl planes may be s-trans and s-trans to the central plane of the 9′-fluorenylidene, yielding the s-trans,s-trans conformation. However, this conformation must be less stable owing to the severe steric repulsion between the two bulky 9- and 9″-fluorenyl groups (plane distance ca. 0.87 Å), so that the possibility of its existence may be excluded from examination of the molecular models.

Consequently, the NMR signal at 4.61 ppm in B arises from the s-trans conformation by analogy with **3**;[9] the other, at 5.36 ppm, is in agreement with that of the singlet in A, and can be assigned as due to the s-cis conformation. Accordingly, compounds A and B must be presumed to be the s-cis,s-cis and s-cis,s-trans conformations, respectively.

The anomalous shifts of aromatic proton signals (5.58, 5.66; 8.26, 8.34 ppm) in the NMR spectra are probably due to a torsional conformation about the $C_{9-9'}$ and $C_{9'-9''}$ sp$^3$–sp$^3$ bonds, so that each 9- and 9″-fluorenyl ring is twisted out from the 9′-fluorenylidene plane to remove the strain within the range of the restricted degree.

Table I
Treatment of 9,9′:9′,9″-Terfluorenyl Isomers with Raney Nickel

| Material | Reaction conditions | | | | Products, g (%) | | | |
|---|---|---|---|---|---|---|---|---|
| (g) | RNi, g | $Et_3N$, g | Temp, °C | Time, hr | B | 3 | 1 | Recovered, g (%) |
| A (1.5) | 10.0 | 0.3 | 60 | 1 | 0.78 (52) | | 0.10 (7) | 0.31 (21) |
| A (1.5) | 10.0 | 0.3 | 60 | 3 | 1.13 (75) | 0.08 (5) | 0.09 (6) | 0.12 (8) |
| A (1.5) | 10.0 | 0.3 | 60 | 5 | 1.14 (76) | 0.04 (3) | 0.10 (7) | 0.05 (3) |
| A (1.5) | 10.0 | 0.3 | Reflux | 3 | 0.42 (28) | 0.28 (19) | 0.58 (39) | |
| A (1.5) | 10.0 | | Reflux | 3 | 0.24 (16) | 0.41 (27) | 0.60 (40) | |
| B (1.5) | 10.0 | 0.3 | 60 | 5 | | 0.53 (35) | 0.09 (7) | 0.60 (40) |
| B (1.5) | 10.0 | 0.3 | Reflux | 3 | | 0.55 (37) | 0.45 (30) | 0.26 (17) |

Thus, two aromatic protons at the 1,8″ positions of the 9- and 9″-fluorenyl planes in A are actually located in the shielding zone of the π electron cloud on the central 9′-fluorenylidene ring, which shifts the signal to higher field; however, the other two protons at the 1″,8 positions are in a deshielded zone which shifts the signal to lower field, as Figure 3 shows. Likewise, the two protons at the 1 and 8 positions of the *cis*-9-fluorenyl ring, with respect to the central 9′-fluorenylidene ring in B, resonate at higher and lower fields than other aromatic protons.

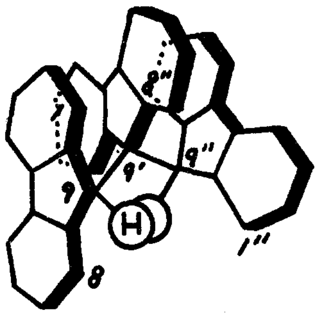


**Figure 3.**

**Isomerization of Rotamer A to B.** No isomerization of A into B except by thermolysis has been performed hitherto. A is also converted into B by treatment with Raney nickel; hydrogenolysis of the resulting B gives **3**, **1**,[10] and a small amount of hexahydrofluorene[11] as shown in Table I.

Upon treating with Raney nickel, A-*9,9″-$d_2$* was converted into B-*9-d* by proton exchange. The terfluorenyl molecule may be adsorbed on the catalyst at the 9″-fluorenyl plane containing a 9″ deuterium atom. Thus, the reaction proceeds with inversion of the conformation to give B-*9-d* by the attack of reactive hydrogen at the back side of the 9″ carbon to which the 9″ deuterium has been attached.

**Michael Addition of Fluorene (1) to 9,9′-Bifluorenylidene (2).** The effect of bases on the formation of these isomers through the Michael addition of **1** to **2** are listed in Table II. The yields of A decreased and those of B increased in the order methyl, ethyl, and *n*-propyl alcohol in the presence of the sodium alkoxide. The predominant formation of A in 90% pyridine–water solution was distinct from the coformation of A and B in sodium ethoxide–dry pyridine, whereupon the ratio of the isomers depends on the polarity of the medium. In addition, the yields of the isomers were inverted as the concentration of sodium ethoxide in ethanol increased.

The Michael addition of 2,7-dibromo-(or chloro-) fluorene to **2** gave abnormal products such as 2,7,2″,7″-tetrabromo- (or chloro-) 9,9′:9′,9″-terfluorenyl by combinations of elimination and readdition steps via 2,7-dihalogeno-9,9′-bifluorenylidene.[12] Therefore, the process for the formation of A and B was investigated by using **1**-*2,7-$d_2$* as a donor. The deuterium contents in A-*2,7-$d_2$* and B-*2,7-$d_2$* are of the same order. Accordingly, the isomers A and B are formed simultaneously through the different sequences, with no retro-Michael reaction occurring, as Scheme II shows.

A could be formed by cis addition involving the cis conformation of the 9-fluorenyl plane with respect to the fluorenylidene plane in **2**. There are two possible ways for the formation of B (s-cis,s-trans) by cis (or trans) addition which includes the s-trans (or s-cis) conformation of the 9-fluorenyl plane with regard to the fluorenylidene plane in **2**. Consideration of models indicates that the protonation

Scheme II

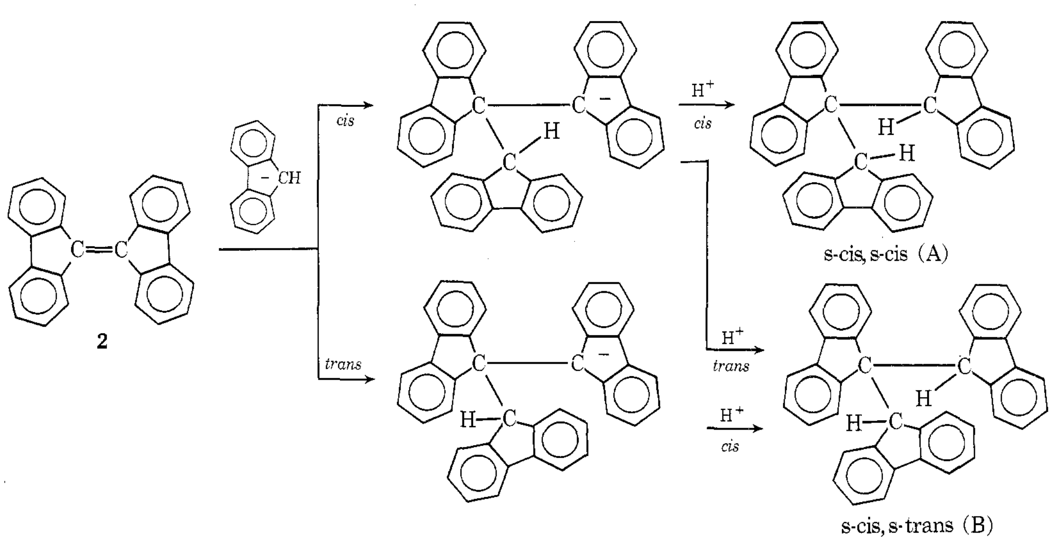


Table II
9,9′:9′,9″-Terfluorenyls by the Michael Addition of 1 to 2

| Reaction conditions | | | | 9,9':9' 9''-Terfluorenyl isomers | | |
|---|---|---|---|---|---|---|
| | | | | Yield of isomers, | Ratio of isomers, % | |
| Solvent | Base | Concn, % | Time, hr | % | A | B |
| EtOH | EtONa | 0.1 | 200 | 78 | 86 | 14 |
| EtOH | EtONa | 1 | 55 | 81 | 68 | 32 |
| EtOH | EtONa | 5 | 30.5 | 62 | 59 | 41 |
| EtOH | EtONa | 10 | 9.5 | 87 | 11 | 89 |
| EtOH | EtONa | 15 | 11 | 84 | | 100 |
| EtOH | EtOK | 0.5 | 150 | 50 | 89 | 11 |
| EtOH | EtOK | 10 | 5 | 87 | 83 | 17 |
| MeOH | MeONa | 1 | 160 | 43 | 74 | 26 |
| MeOH | MeONa | 10 | 53 | 72 | 100 | |
| MeOH | MeOK | 1 | 200 | 30 | 100 | |
| MeOH | MeOK | 10 | 51 | 80 | 100 | |
| *n*-PrOH | *n*-PrONa | 1 | 52 | 82 | 25 | 75 |
| *n*-PrOH | *n*-PrONa | 10 | 45 | 56 | | 100 |
| Pyridine | EtONa | 1 | 15 | 74 | 56 | 44 |
| Pyridine | KOH | 5 | 3 | 80 | 100 | |

of the latter course is more hindered than those of the former resulting from the close proximity of the 9″-fluorenyl plane.

## Experimental Section

All the melting points are uncorrected. The melting points of deuterio compounds in this series are identical with those of the parent hydrocarbons.

The VPC analyses were run with a JGC-1100FP gas chromatograph (Japan Electron Optics Laboratory Co., Ltd.), using a 1-m column containing 3% Silicone DC QF-1 on Chromosorb W AW (60–80 mesh). The content of each component was calculated from the peak areas as the average value of five chromatograms. Response factors used to correlate relative areas with percent yields of hexahydrofluorene and 1 were 0.84 and 1.00.

The ir spectra were obtained as KBr pellets (4000–400 cm$^{-1}$) or as suspensions in hexachlorobutadiene (3000–2800 cm$^{-1}$) using a IR-G spectrophotometer (Japan Spectroscopic Co., Ltd.).

The Raman spectra were recorded on a JRS-U1 spectrometer (Jeol) with an argon laser (5145.4 Å) and an interference filter. The experiments were run with a slit width of 160 $\mu$ and 23 A of laser output at a scanning speed of 10 Å/min.

The mass spectra were measured with a RMU-6E apparatus (Hitachi, Ltd.). The sample evaporating temperature was controlled at 160° (for monomeric fluorenes) or 200° (for dimeric and trimeric fluorenes). Calculation of incorporated deuterium into compounds was from the average value of five spectra.

The NMR spectra were obtained with a JNM-PS-100 (100 MHz) or a JNM-C60-HL (60 MHz) spectrometer (Jeol) in benzene-$d_6$ (for dimeric and trimeric fluorenes) or $CCl_4$ (for monomeric fluorenes), using TMS as internal reference. The deuterium incorporation was determined from the average value of seven peaks.

**Treatment of 9,9′:9′,9″-Terfluorenyl Isomers with Raney Nickel. Typical Procedure.** To a mixture of 1.5 g of A and 100 ml of dry toluene was added 10.0 g of Raney nickel (W-4), 0.3 g of triethylamine, and 10 ml of dry toluene, which was maintained at 60° for 3 hr while being stirred.

The reaction mixture was filtered and the filtrate was evaporated under reduced pressure; the residue was extracted with 100 ml of boiling ethanol, leaving a powder which was recrystallized from 200 ml of ethyl acetate to give B (1.08 g), mp 256–257° dec, recovered A (0.12 g, 8%), mp 291–293° dec, and **3** (0.06 g), mp 242–243°.

Upon standing, the alcohol extract gave 0.05 g (total 1.13 g, 75%) of B, mp 254–256° dec. The mother liquor was concentrated to dryness, and the residue was sublimed in vacuo at 130°. The sublimate was recrystallized from ethanol to yield **1** (0.09 g), mp 110–113°. **3** (0.02 g, total 0.08 g, 5%) was obtained by recrystallization of the residue. The alcohol mother liquor was submitted to VPC; **1** and 1,2,3,4,4a,9a-hexahydrofluorene were confirmed.

**Treatment of Fluorene (1) with Raney Nickel.** A mixture of 5.0 g of **1** and 3.0 g of triethylamine in 100 ml of dry toluene was refluxed with 25 g of Raney nickel for 5 hr. The reaction mixture was analyzed by VPC; 40% of 1,2,3,4,4a,9a-hexahydrofluorene and 60% of **1** were confirmed.

The toluene was removed in vacuo to leave a faintly colored oil which was distilled to give hexahydrofluorene as a colorless liquid: bp 128–130° (15 mm), 264° (757 mm) (the Siwoloboff method); $n^{20}\text{D}$ 1.5536; $d_4^{20}$ 1.008; $(R_L)_D$ 54.72 (calcd, 54.61); ir (KBr sandwich) 679, 732, 748, 762, 1445, 1471, 2870, 2950, 3020, 3045, and 3070 cm$^{-1}$; mass spectrum *m/e* 172 ($M^+$), 166, 157, 143, 129, 115, 104, 91, 89, and 77; NMR $\delta$ 0.81–2.01 (m, 8 H), 2.11–3.31 (m, 4 H), and 7.03 ppm (s, 4 H).

**Michael Reaction of 9,9′-Bifluorenylidene (2) with Fluorene (1). Typical Procedure.** Sodium (1.7 g) was treated with 54 ml of absolute ethanol; then there was added 1.1 g ($^{1}/_{300}$ mol) of **2** and 0.6 g ($^{1.1}/_{300}$ mol) of **1**, the mixture was heated in a sealed tube at 95–98° for 9.5 hr.

After cooling, the precipitate was filtered off and recrystallized from benzene and/or ethyl acetate to give B (1.02 g), mp 256–257° dec. The filtrate was added to water, and the precipitate was separated and further purified by a combination of recrystallization, alumina column chromatography, and vacuum sublimation. Subsequently, 0.25 g (total 1.27 g, 77%) of B, mp 256–257° dec, 0.16 g (10%) of A, mp 291–293° dec, trace amounts of fluorenone, mp 80–82°, and **1**, mp 113–115°, were obtained.

In case ethanol was used as solvent, the crystals of B were contaminated by 1,4-bis(2,2′-biphenylylene)-1,3-butadiene.[13] The butadiene was removed easily as a complex with 2,4,7-trinitrofluorenone, mp 297–298.5° dec.

Anal. Calcd for $C_{28}H_{18}\cdot 2(C_{13}H_5O_7N_3)$: C, 65.86; H, 2.87; N, 8.53. Found: C, 65.79; H, 2.61; N, 8.42.

Beside 9,9′:9′,9″-terfluorenyl isomers, in some experiments, trace amounts of **3**, fluorenol, and fluorenone were separated. A minute amount of 9-methoxy-9,9′-bifluorenyl, mp 155–157°, was isolated instead of **3** in the presence of potassium methoxide.

Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.69; H, 5.46.

**Synthesis and Reaction of A-*9,9″-d*$_2$. 1-*9,9-d*$_2$.** The title compound was prepared according to the directions of Cram and Kollmeyer.[14] The extent of deuterium incorporation was 95% by NMR: mass spectrum *m/e* 167 ($d_1$, 12%) and 168 ($d_2$, 88%).

**3-*9,9′-d*$_2$.** **3** was deuterated in a similar manner to give the deuterio compound (98% yield). Deuterium incorporation was calculated as 100% by NMR; mass spectrum *m/e* 332 ($d_2$, 100%).

**B-*9,9″-d*$_2$.** A mixture of 1.64 g of **2** and 0.92 g of **1**-*9,9-d*$_2$ in 30 ml of ethanol-*O-d* containing 3 g of sodium ethoxide was heated and gave 1.83 g (74%) of B-*9,9″-d*$_2$ and 0.14 g (6%) of A-*9,9″-d*$_2$. Deuterium content of B was accounted for as 100% on the 9 and 9″ positions (there were no peaks at 5.36 and 4.61 ppm) by NMR: mass spectrum *m/e* 494 ($d_0$, 0.1%), 495 ($d_1$, 13.9%), and 496 ($d_2$, 86%).

**A-*9,9″-d*$_2$.** **2** was treated with **1**-*9,9-d*$_2$ in a mixture of sodium deuteroxide, deuterium oxide, and pyridine to give A-*9,9″-d*$_2$ (83% yield). A deuterium content of 89% at the 9 and 9″ positions (5.36 ppm) was determined by NMR: mass spectrum *m/e* 494 ($d_0$, 0%), 495 ($d_1$, 19%), and 496 ($d_2$, 81%).

**Treatment of A-*9,9″-d*$_2$ with Raney Nickel.** A-*9,9″-d*$_2$ (1.50 g) was allowed to react with Raney nickel and yielded 0.42 g (28%) of B-*9-d* and 0.80 g (53%) of A-*9,9″-d*$_2$. A 90% deuterium content at the 9 and 9″ positions (5.36 ppm) of recovered A was observed by NMR: mass spectrum *m/e* 494 ($d_0$, 1%), 495 ($d_1$, 16%), and 496 ($d_2$, 83%). The content of unexchanged deuterium at the 9 (ca. 94%, 5.36 ppm) and 9″ positions (ca. 25%, 4.61 ppm) of B was estimated by NMR: mass spectrum *m/e* 494 ($d_0$, 20%), 495 ($d_1$, 59%), and 496 ($d_2$, 21%).

**Michael Reaction of 2 with 1-*2,7-d*$_2$. 1-*2,7-d*$_2$.** A mixture of 12.54 g of 2,7-diiodofluorene and 9.7 g of lithium aluminum deuteride in 150 ml of dry tetrahydrofuran was refluxed for 9 hr.[15] The reaction mixture was decomposed with 9 ml of deuterium oxide in 20 ml of dry tetrahydrofuran and concentrated to dryness. The residue was sublimed in vacuo at 90° to afford 2.5 g (50%) of **1** (from *n*-hexane).

A mixture of 2.5 g of foregoing **1**, 2 g of sodium methoxide, 20 ml of water, and 80 ml of 1,2-dimethoxyethane was refluxed for 15 hr. Work-up of the resulting mixture gave **1**-*2,7-d*$_2$ (2.22 g): mass spectrum *m/e* 166 ($d_0$, 33%), 167 ($d_1$, 44%), 168 ($d_2$, 22%), and 169 ($d_3$, 2%).

**Michael Reaction of 2 with 1-*2,7-d*$_2$.** Foregoing **1**-*2,7-d*$_2$ (0.37 g) was allowed to react with **2** (0.66 g) to give B (0.54 g) and A (0.02

g). A: mass spectrum *m/e* 494 ($d_0$, 20%), 495 ($d_1$, 39%), 496 ($d_2$, 33%), and 497 ($d_3$, 9%). B: mass spectrum *m/e* 494 ($d_0$, 19%), 495 ($d_1$, 40%), 496 ($d_2$, 32%), and 497 ($d_3$, 9%).

**Michael Reaction of 2 with 1-*1-d*. 1-Iodofluorene.** A 0.9-g portion of 1-aminofluorene[16] was diazotized in the usual way and the diazonium sulfate was decomposed in the presence of potassium iodide to yield 1-iodofluorene (0.39 g, 27%), mp 40–42°, mass spectrum *m/e* 292 ($M^+$) and 165.

Anal. Calcd for $C_{13}H_9I$: C, 53.45; H, 3.11. Found: C, 53.66; H, 2.94.

The title compound was oxidized with sodium bichromate in acetic acid to afford 1-iodofluorenone, mp 143.5–145° (lit.[17] mp 144–145°).

**1-*1-d*.** 1-*1-d* was obtained from 1-iodofluorene in an analogous manner from that of 1-*2,7-$d_2$*: mass spectrum *m/e* 166 ($d_0$, 26%), 167 ($d_1$, 63%), and 168 ($d_2$, 11%).

**Michael Reaction of 2 with 1-*1-d*.** A mixture of 2 and 1-*1-d* was treated as usual and afforded A-*1-d* (12% yield) and B-*1-d* (63% yield). A-*1-d*: mass spectrum *m/e* 494 ($d_0$, 35%), 495 ($d_1$, 57%), and 496 ($d_2$, 8%). B-*1-d*: mass spectrum *m/e* 494 ($d_0$, 36%), 495 ($d_1$, 60%), and 496 ($d_2$, 4%).

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**Registry No.**—1, 86-73-7; 2, 746-47-4; 3, 1530-12-7; A, 42759-04-6; B, 42759-03-5; hexahydrofluorene, 1559-97-3; 1,4-bis(2,2′-biphenylylene)-1,3-butadiene complex with 2,4,7-trinitrofluorenone, 54366-31-3; 9-methoxy-9,9′-bifluorenyl, 54366-32-4; 1-iodofluorene, 54366-33-5.

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# Conformations of Vicinal Diesters

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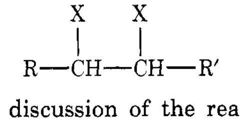
In diesters derived from 4-methyl-2,3-pentanediol, 1-phenyl-1,2-propanediol, and 3-methyl-1-phenyl-1,2-butanediol, the preference for gauche oxygen functions with respect to the ethanic backbone is nearly as large as for the diols themselves. Two reasons for the preference for gauche diester groups are possible: (a) dipolar attraction and (b) an intrinsic attraction related to electronegativity, but presently not well defined. Solvent effects and the effects of steric hindrance on conformation were studied, as well as $^{13}C$ chemical shifts and $^{13}C$–H coupling constants. For erythro diesters, the data seem best interpreted in terms of an intrinsic attraction.

In their classic work on the application of NMR to problems in conformational analysis, Bothner-By and Naar-Colin observed rather unusual conformations for *meso*-2,3-diacetoxybutane (gauche ester functions).[1] Electrostatic attraction between the dipoles of the ester groups was considered to be a possible reason for this conformational preference. Later Schmid also reported unusual conformations for phenyl-substituted diesters.[2] However, substituted succinates show no well-defined preference for gauche carbonyl functions.[3,4]

Recent work by Abraham and Kemp showed that vicinal fluorine groups X preferred a gauche orientation despite sizable dipolar repulsion.[5] Phillips and Wray have correlated the tendency for X groups to occupy a gauche conformation with the total electronegativity of these groups.[6] However, Eliel and Kaloustian attributed the tendency for vicinal ether functions to be gauche to an attractive van der Waals interaction.[7] It is possible that electronegative X groups shrink the "size" of their respective lone pairs[8] so that the repulsions of the lone pairs is superseded by electron–nuclear attractions.[6,9] However, others have warned against too facile arguments involving the size of lone pairs.[8]



$$\begin{array}{c} \quad\ \ \mathrm{X}\quad\ \ \mathrm{X} \\ \quad\ \ |\quad\ \ \ | \\ \mathrm{R{-}CH{-}CH{-}R'} \end{array}$$

In a theoretical discussion of the reason for gauche X groups in 1,2-difluoroethane, Pople et al. considered the interaction of the two X groups to be repulsive, but this effect was counteracted by a hyperconjugative effect such that the electron withdrawal by an electronegative group X "partially empties the 2p orbital on carbon and facilitates the hyperconjugative electron delocalization by the neighboring $CH_2$ group".[10] On the other hand, Epiotis considers the interaction of two X groups to be attractive due to interaction of nonbonding pairs on the X groups forming antibonding and bonding combinations. The destabilizing ef-