Tetrahedron Letters No. 16, pp 1541 - 1544, 1974. Pergamon Press. Printed in Great Britain.

STABLE RESTRICTED ROTATION ISOMERS ABOUT THE SP^3-SP^3 CARBON-CARBON BONDS IN 9,9':9',9"-TERFLUORENYLS AT ROOM TEMPERATURE

Kazuo Suzuki and Masahiro Minabe
Department of Industrial Chemistry, Faculty of Technology, Utsunomiya
University, Ishii-cho, Utsunomiya, 321-31 Japan

(Received in Japan 21 February 1974; received in UK for publication 12 March 1974)

During the syntheses of fluorene derivatives, we have obtained by the following reactions two kinds of rotational isomers which are stable at room temperature in solution.

Compound (A) mp 293°C(dec) was first obtained by Pinck and Hilbert$^{1)}$ on the Michael reaction of 9,9'-bifluorenylidene (1) with fluorene, and compound (B) mp 257°C(dec)$^{2)}$ was also obtained by treatment of fluorene with sodamide. Both compounds $C_{39}H_{26}$ give fluorenone by oxidation and fluorene by reduction.

A was converted into B and 1, and B gave 9,9'-bifluorenyl (2) and 1 at their melting points$^{2)}$; the formation of these pyrolysates have been established by ESR$^{3)}$ as resulting by way of radical pathways. Both A and B were obtained simultaneously by reaction with 9-bromofluorene in methanolic potassium hydroxide-acetone and by other reactions$^{4)}$, and we suggested that A and B could be the rotational isomers around the C_9-$C_{9'}$-$C_{9''}$ single bonds$^{5)}$.

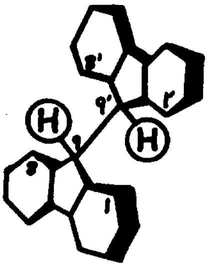
In this paper, we wish to present additional experimental results, and propose the spatial structures of A and B on the basis of their chemical and spectral grounds. A gave B by treatment with Raney-nickel (76 %) and with $LiAlH_4$ (13 %). Furthermore, B was converted into A by reaction with NBS (56 %) and with triton B (42 %). Both were interconverted, A into B (23 %) and B into A (16 %), by reaction with $NaAlH_2(OCH_2CH_2OCH_3)_2$.

The IR spectra(hexachlorobutadiene) of two methines absorbed at 2899 cm^{-1} for 2 (9-CH, 9'-CH) and at 2917 cm^{-1} in singlet for A (9-CH, 9"-CH), whereas absorptions at the two bands of 2883 and 2918 cm^{-1} were observed for B (9-CH, 9"-CH). Similarly, both methines fairly strongly absorbed in the Lasser-Raman spectra (powder; Ar^+, 5145.5 Å) at 2900 cm^{-1} for 2, at 2918 cm^{-1} for A, and at 2884 and 2919 cm^{-1} in two bands for B, respectively.

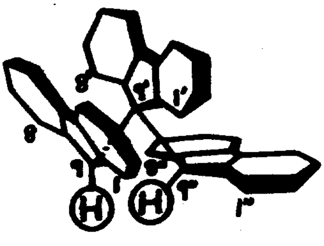
Mass spectra of A and B are virtually identical, the parent peak is small at m/e 494 (M^+), and the base peak at m/e 329 (9,9'-bifluorenyl cation) and m/e 165 (9-fluorenyl cation) are fragments whose origin can be interpreted by simple cleavage of $C_{9-9'}$ or $C_{9'-9''}$ bonds from the parent ion.

The NMR spectrum (100 MHz, C_6D_6) of 2 exhibits 16 proton signal at 7.58-6.85 ppm (aromatic region) and two proton singlet of the 9- and 9'-methines at 4.61 ppm. However, 1[6] gives a multiplet in the low field (8.31 ppm) due to the steric interaction between 1,8- and 1',8'-hydrogen atoms, and the rotation about $C_{9-9'}$ for 2[6,7] is fairly free at room temperature. Both A and B show 24 proton signal at 8.34-5.58 ppm (aromatic region), and exhibit two proton singlet of C_9 and $C_{9''}$ at 5.36 ppm in A, and non-equivalent two protons at 4.61 and 5.36 ppm in B. And the signal 4.61 ppm is indicates that arise from conformation 2, and other, 5.36 ppm, is in agreement with that of singlet in A, thus data on NMR, IR, and Raman can be interpreted on the basis of assuming that the partial conformation of B consist of the s-trans conformation 2. In addition, these methine protons in 2, A, and B were assigned by syntheses of the corresponding deuterated compounds.

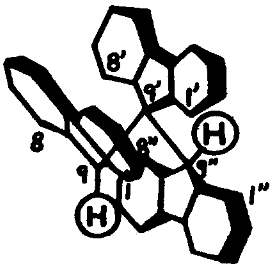
An examination of space-filling molecular models of 9,9':9',9"-terfluorenyls indicates that the rotation about the SP^3-SP^3 single bonds of $C_{9-9'}$ and $C_{9'-9''}$ are sufficiently restricted due to the close proximity of the hydrogen atoms in 1,8,1',8',1",8",9, and 9" carbon atoms, and the following rotamers can, in ground state, exist in three forms as Fig.



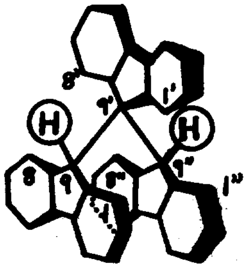
s-trans (2)



s-cis,s-cis



s-cis,s-trans



s-trans,s-trans

The above represents three approximate ground state conformations proposed for 9,9':9',9"-terfluorenyls: *s-cis*,*s-cis*; *s-cis*,*s-trans*; and *s-trans*,*s-trans*.

a) Three planes of 9- and 9"-fluorenyls and 9'-fluorenylidene are *cis*-folded with respect to one another, and the molecule is called the *s-cis*,*s-cis* conformation.

b) Both planes of 9-fluorenyl and 9'-fluorenylidene are *cis*-folded with respect to each other, and 9"-fluorenyl is displaced *s-trans* to the central 9'-fluorenylidene, and is called the *s-cis*,*s-trans* conformation.

c) Two planes of 9- and 9"-fluorenyls are displaced *s-trans* and *s-trans* to the central plane of the 9'-fluorenylidene, respectively and is called the *s-trans*,*s-trans* conformation.

Whereas the third conformation (*s-trans*,*s-trans*) 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), the possibility of this may be neglected from the results of examination of the molecular models. Consequently, the signal at 5.36 ppm in B should be assigned to the *s-cis* conformation. Accordingly, compounds A and B must assume with the *s-cis*,*s-cis* and *s-cis*,*s-trans* conformations, respectively.

In addition, the 9- (or 9"-) fluorenyl plane in *s-cis* is inclined with respect to the central 9'-fluorenylidene plane at an angle of about 70° based on the atomic-radius and -angle in ground state. As B is somewhat more stable than A toward thermal decomposition, it seems to be the reason for the spatial arrangement of the three bulky groups being held as far from one another as possible.

While, some characteristic aromatic shifts appear in considerably lower- and higher-fields as two sets of doublets at 5.58 and 5.66 ppm, and at 8.26 and 8.34 ppm in A and B, and each peak is equal to one proton in A and half proton in B, respectively. Accordingly, these anomalous shifts are probably due to the trans-twisted out of the 9- and/or 9"-fluorenyl plane to release the strain within the range of the restricted degree about the SP^3-SP^3 bonds. Thus, the conformation of any two aromatic protons in the 1,8" or 1",8 positions on the 9- and 9"-fluorenyl planes in A which are held over and below with respect to the central 9'-fluorenylidene plane and lead to increased shielding of these protons, whereas the other two protons are removed from the central fluorenylidene ring-current area to remain uneffected and these are influenced by a deshielding effect which shifts to lower fields. Under the same treatment, it can be regarded as being analogous to the two protons at the 1 and 8 positions on the 9-fluorenyl group in B.

Consequently, the conformational isomers of 9,9':9',9"-terfluorenyls are due solely to restriction of rotation about single bonds, *viz*, *s-cis*,*s-cis* (A) and *s-cis*,*s-trans* (B) as shown in Fig.

Acknowledgement:

We are grateful to Dr. M. Ōki of the Tokyo University for his valuable discussions.

References:

1. L. A. Pinck and G. E. Hilbert, *J. Amer. Chem. Soc.*, 68, 2014 (1946).
2. K. Suzuki, *Nippon Kagaku Zasshi*, 70, 189 (1949).
3. K. Suzuki, M. Minabe, S. Kubota, and T. Isobe, *Bull. Chem. Soc. Japan*, 43, 2217 (1970).
4. K. Suzuki and S. Kajigaeshi, *ibid.*, 35, 408 (1962); K. Suzuki, *Nippon Kagaku Zasshi*, 75, 711 (1954); S. Kajigaeshi, *ibid.*, 82, 1397 (1961).
5. K. Suzuki, *Technol. Repts. Tohoku Univ.*, 19, 63 (1955).
6. M. Rabinovitz, I. Agranat, and E. D. Bergmann, *Tetrahedron Lett.*, 1965, 1265; G. P. De Gunst, *Rec. trav. chim., Pays-Bas*, 88, 801 (1969).
7. K. D. Bartle, P. M. G. Bavin, D. W. Jones, and R. L'amie, *Tetrahedron*, 26, 911 (1970).