Reactivities of Stable Rotamers. XXXI. Bromine Addition to the Olefinic Moiety of Rotameric 1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalenes[1)]

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Reaction of bromine with the *ap* form of the title compound afforded a normal addition compound, whereas the same with the *sp* form did no addition compound but a pair of bromo-olefins and a cyclized product, formation of which can be rationalized by deprotonation from and by attack of the π-system of the fluorene group on the intervening cation. The abnormal reactions of the *sp* form are the consequence of the steric effects of the fluorene moiety that prohibits the formation of the tetrahedral carbon at the reaction site. The stereochemistry of the cyclized product was determined both by NOE experiments and by X-ray crystallography. The stereoselective formation of only one isomer was rationalized by the structure of the starting material, of which stereodynamics was studied by the dynamic NMR method, and the direction of the attack of the bromine cation. For comparison of the fate of the intervening cation, the adduct from the *ap* form was treated with silver *p*-toluenesulfonate. It was found that the ratios of olefin formation were different from one rotamer to another. The results are discussed on the basis of different degree of openness of the intervening bromonium cation with reference to the same reaction for (1,2-dibromo-1-methylethyl)benzene.

Various addition reactions to the ethenyl group in 2-ethenyl-1-(9-fluorenyl)naphthalene (**1**) rotamers were examined to find that the differences between a pair of rotamers were rather small: The factor was ca. 2 at the most.[2)] The small difference may be attributed to the coplanar structure of the ethenyl group with the naphthalene ring in **1**, as revealed by the ultraviolet spectra of these isomers, because in that very structure the ethenyl group in the *sp* form is placed in such a way that the attack for addition reactions can take place without significant steric effects (Chart 1).

The *sp*-isomer of 1-(9-fluorenyl)-2-(1-methylethenyl)-naphthalene (**2**) is expected to provide a quite different situation. If an addition reaction were to take place to the 1-methylethenyl group, the carbon atom that is directly connected to the naphthalene ring must take an sp^3-hybridized structure with three nonhydrogen substituents. This should offer prohibitive steric effects to exist.[3)] Failure of addition reactions to the carbonyl group to take place, except a formyl, in the *ap* form of 2-acyl-1-(9-fluorenyl)naphthalene (**3**), though they are easy for the *sp* rotamer,[4)] can be attributed to this effect.

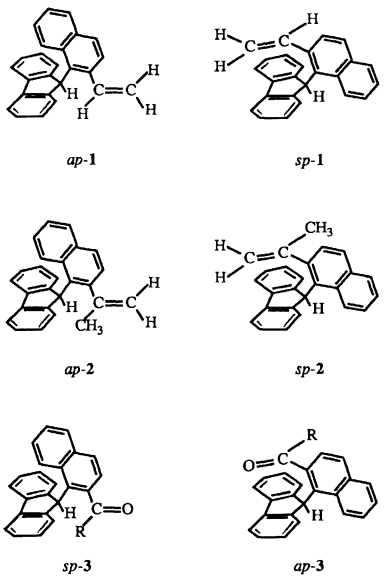


Chart 1.

An intermediate formation by attack of a bromine cation on the ethenyl group in *sp*-**2** will take place, however. In the sterically crowded olefins, treatment of them with bromine is known to produce rearranged products[5)] or brominated olefins which are formed by deprotonation of an intervening bridged bromonium cation.[6)] It was reported recently that a sterically congested olefin underwent addition of bromine but lost hydrogen bromide easily at 0°C.[7)] The same or similar situation will occur in the case of *sp*-**2**. Then it will provide another example that shows quite different properties in reactions among rotational isomers, because the *ap* isomer is expected to give a normal addition product due to the fact that the ethenyl group in this conformation is open to the attack of a bromine molecule. Thus we decided to examine addition reactions of bromine to the ethenyl group of compound **2** rotamers.

Synthesis and Barrier to Rotation. The synthesis of the *ap*-isomer (**2**) was straightforward, because preparation of *sp*-1-(9-fluorenyl)-2-naphthalenecarboxylic acid (**4**) in large quantity was reported.[8)] Grignard addition of methylmagnesium iodide to the corresponding methyl ester (**5**) afforded the corresponding tertiary alcohol (**6**) in a fair yield. The relatively inferior results are due to the fact that some isomerization to the *ap* form takes place under the conditions owing to the acidic nature of the 9-CH group. The alcohol (**6**) was dehydrated with pyridinium *p*-toluenesulfonate to the

desired *ap*-olefin (**2**).

Isomerization of *ap*-**2** to *sp*-**2** was expected to pose a difficulty because the *sp* isomer must be an unstable one and in normal equilibration the *ap* form will dominate. We decided to overcome this problem by taking advantage of the solvation effect in the lithium salts. If we derive a lithium salt from *ap*-**2** in ether, the ether will solvate the lithium and the steric bulkiness of the solvated ion may surpass that of the 1-methylethenyl group in the *sp*-position. Then we can hope that the *sp* form dominates in the equilibrium. In reality, we performed the lithiation of *ap*-**2** with butyllithium in 1, 2-dimethoxyethane. After heating the lithiated product for 2 h and quenching the salt with aqueous acetic acid, we obtained a ca. 1:1 mixture of the *ap*- and *sp*-rotamers. They could be separated by chromatography (Chart 2).

In order to verify that we really see the reactivity of the rotational isomers, we first determined the rotational barrier. The rates of isomerization were measured for a solution of the *sp*-rotamer in toluene-d_8 at 80.5°C. We started from this isomer because we expected that this isomer would be a minor component at equilibrium and that measuring the rates of isomerization of this isomer should give more accurate value than starting from the stable isomer. Indeed, the population ratio, *ap*/*sp*, was 15.6 at equilibrium at that temperature and the rate constant for isomerization was $(7.7\pm0.5)\times10^{-5}$ s^{-1}. Free energy of activation for rotation was calculated to be 27.5 kcal mol^{-1} (1 cal=4.184 J). Thus, if a reaction is carried out at a temperature lower than 50°C, we may claim that we are really seeing the reactivity of the rotamers.

Bromination and Products. Addition of bromine across the olefin bond in *ap*-**2** was carried out in carbon tetrachloride. The reaction was rather slow, as indicated by fading of the color of bromine. The product was a normal adduct, 2-(1,2-dibromo-1-methylethyl)-1-(9-fluorenyl)naphthalene (*sp*-**7**), however. No other product was detected.

In contrast, addition of bromine to *sp*-**2** in carbon tetrachloride causes evolution of a copious amount of hydrogen bromide and fading of the bromine color was fast. Product analysis indicated that there were two types of olefins (*ap*-**8** and *ap*-**9**) that contain bromine and a cyclized product (**10**). The average yields of the products, normalized to 100%, are given in the scheme with the structures (Chart 3).

The structures of the olefins were determined by spectroscopic evidence. ^{1}H NMR spectra of compound *ap*-**8** showed a methylene proton signal at a relatively low field and two signals due to terminal olefins, whereas that of *ap*-**9** did a signal due to a methyl group and an olefinic proton. No NOE enhancement was observed between the methyl and the olefinic protons. This is a basis of the assignment of the *E*-structure of the olefin. The *Z*-isomer of the olefin was not detected.

The structure of **10** was assigned first by spectroscopic evidence and by considering the reaction mechanisms. It had a signal due to a methyl group and that due to a bromomethyl group. It also had a signal due to a proton corresponding to the 9-H of 9-arylfluorenes but an aromatic proton was missing. If we consider an intervening cation (**11**), it is natural to assign the structure **10**, because attack of the cationic center on the fluorene ring will produce the compound.

To the first approximation,[9] in both isomers of **2**, attack by bromine cation on the π-system will produce bromomethyl cations (**11** and **12**), either bridged or unbridged. **11** is written in the form of the unbridged and **12** in bridged (Chart 4). Though detailed reasons for these pictures are given in a later section of this paper, these structures explain the observed phenomena easily. The open cation (**11**) may lose a proton to produce the olefins (**8** and **9**) and form the cyclized compound

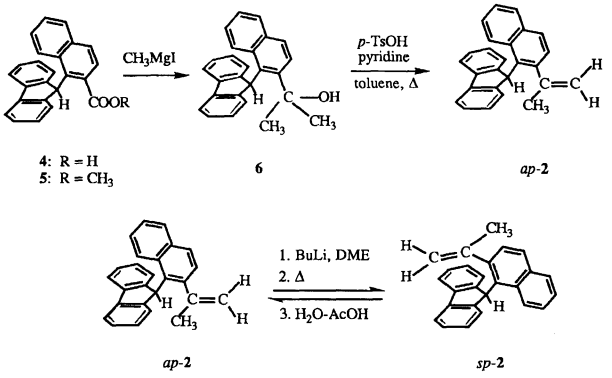


Chart 2.

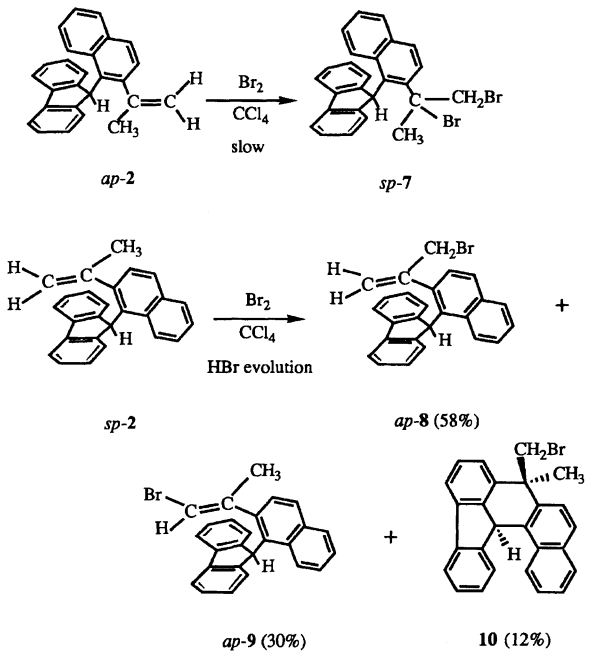


Chart 3.

11 12

Chart 4.

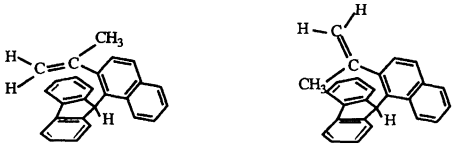
(**10**) by attack of the π-system on the carbon-cationic center. By contrast, the bridged bromonium ion **12** is slow in giving up a proton and is attacked by Br_3^- ion to form the dibromide (*sp*-**7**), formation of which is slow because the back side of the bromonium ion is blocked by the fluorene ring.

It is interesting to note that no stereoisomer of **10** was formed. Assignment of stereochemistry of compound **10** was tentative but had the following rationalization. That is, if the conformation of compound *sp*-**2**, having the naphthalene ring tilted from the bisecting plane of the fluorene ring,[10] is considered, the olefin-inside form (**13**) should be more stable than the olefin-outside form (**14**) because of the steric effect (Chart 5). If *sp*-**2** reacts in such a conformation with a bromine cation, the bromomethyl group is formed over the fluorene ring and if the cation reacts with the π-system before rotation, the product should be **10**, rather than the isomer in which the bromomethyl and methyl groups are stereochemically reversed.

Structure of Olefins 2. In order to confirm this consideration and to get further insight into the outcome of the reactions, we studied the structures of *ap*-**2** and *sp*-**2** and of the cyclized product by other methods.

UV absorption spectra of *ap*-**2** and *sp*-**2** indicated that absorptions seen at long wave lengths for *sp*- and *ap*-**1** were missing. Instead there were absorptions at shorter wave lengths than **1**. These indicate that the ethenyl group in compound **2** are indeed not coplanar with the naphthalene ring in both conformers.

MMP2 calculations indicate that the stable structures of *ap*- and *sp*-**2** have, as expected from the UV spectra, the ethenyl group nonplanar with the naphthalene ring. In addition, the MMP2 calculations show that, of the two conformations of *sp*-**2** (**13** and **14**), conformation **13** is more stable than **14** by ca. 2 kcal mol^{-1}. This indicates that conformation **14** is practically nonexistent. The difference in steric energy of the stable form (**13**) of *sp*-**2** from that of *ap*-**2** amounts to 2.0 kcal mol^{-1} in agreement with the observed difference from the equilibrium (1.9 kcal mol^{-1}). However, MMP2 calculations may fail to exactly predict the stabilities of such isomers as are treated here, because the steric situation is very severe in these molecules.



13 14

Chart 5.

Thus we decided to perform X-ray crystallography of the olefins (**2**). Unfortunately, *ap*-**2** has not crystallized into a suitable form for X-ray crystallography but *sp*-**2** did. Atomic coordinates and an ORTEP drawing of the molecule are given in Table 1 and Fig. 1, respectively. Numberings of carbon atoms are also given in Fig. 1. The olefinic side chain in the *sp*-**2** molecule is indeed nonplanar with the naphthalene ring, the torsion angle being ca. 70° (see Table 3). The average plane of the 1-methylethenyl group is not strictly parallel with the fluorene ring but is tilted to a small extent.

The stable form in crystals of *sp*-**2** is indeed the olefin-inside form (**13**), as expected from empirical considerations and from MMP2 calculations. Of the three carbons consisting the 1-methylethenyl group in *sp*-**2**, the

Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Patrameters with Estimated Standard Deviations in Parentheses for *sp*-1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene (*sp*-**2**)

Atom	x	y	z	B_{eq}
C(1)	2677(1)	3654(1)	8015(1)	5.24(4)
C(2)	2546(1)	4756(1)	7519(1)	6.14(5)
C(3)	1706(1)	5483(1)	7464(1)	6.31(5)
C(4)	974(1)	5133(1)	7893(1)	5.61(4)
C(4a)	1098.8(9)	4029(1)	8392.4(9)	4.44(3)
C(4b)	479.4(9)	3436(1)	8930(1)	4.52(3)
C(5)	−396(1)	3806(1)	9144(1)	5.86(4)
C(6)	−770(1)	3086(2)	9756(1)	6.79(5)
C(7)	−285(1)	2011(2)	10151(1)	6.52(5)
C(8)	577(1)	1622(1)	9927(1)	5.49(4)
C(8a)	952.9(9)	2336(1)	9314.5(9)	4.33(3)
C(9)	1881.1(9)	2132(1)	8972(1)	4.36(3)
C(9a)	1954.1(9)	3304(1)	8454.6(9)	4.28(3)
C(1′)	2903.6(9)	1606(1)	9862(1)	4.58(3)
C(2′)	3629.2(9)	2279(1)	10716(1)	4.94(3)
C(3′)	4601(1)	1752(2)	11496(1)	6.77(5)
C(4′)	4801(1)	583(2)	11431(2)	7.94(6)
C(4a′)	4059(1)	−138(2)	10610(2)	7.16(6)
C(5′)	4251(2)	−1376(2)	10569(2)	10.3(1)
C(6′)	3516(3)	−2062(2)	9770(3)	12.2(1)
C(7′)	2573(2)	−1576(2)	8981(2)	10.5(1)
C(8′)	2365(2)	−404(1)	8933(2)	7.49(6)
C(8a′)	3103(1)	365(1)	9811(1)	5.85(4)
C(1″)	3468(1)	3552(1)	10894(1)	5.04(4)
C(2″)	2728(1)	3899(1)	11245(1)	5.73(4)
C(3″)	4250(2)	4394(2)	10736(2)	7.92(6)

Table 2. Selected Bond Angles in Compound *sp*-**2**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(8a)	C(9)	C(9a)	102.3(1)	C(3′)	C(2′)	C(1″)	116.4(1)
C(8a)	C(9)	C(1′)	115.7(1)	C(2′)	C(1″)	C(2″)	121.5(1)
C(9a)	C(9)	C(1′)	119.0(1)	C(2′)	C(1″)	C(3″)	116.0(1)
C(1′)	C(2′)	C(3′)	119.2(1)	C(2″)	C(1″)	C(3″)	122.3(1)
C(1′)	C(2′)	C(1″)	124.3(1)				

Table 3. Selected Torsion Angles in Compound *sp*-**2**

Atom-Atom-Atom-Atom	Angle/°	Atom-Atom-Atom-Atom	Angle/°
C(9a)–C(9)–C(1′)–C(8a)	−136.7	H(9)–C(9)–C(1′)–C(2′)	163.6
C(9a)–C(9)–C(1′)–C(2′)	44.2	C(2″)–C(1″)–C(2′)–C(1′)	70.8
C(8a)–C(9)–C(1′)–C(8a′)	101.0	C(2″)–C(1″)–C(2′)–C(3′)	−109.0
C(8a)–C(9)–C(1′)–C(2′)	−78.2	C(3″)–C(1″)–C(2′)–C(1′)	−113.8
H(9)–C(9)–C(1′)–C(8a′)	−17.2	C(3″)–C(1″)–C(2′)–C(3′)	66.5

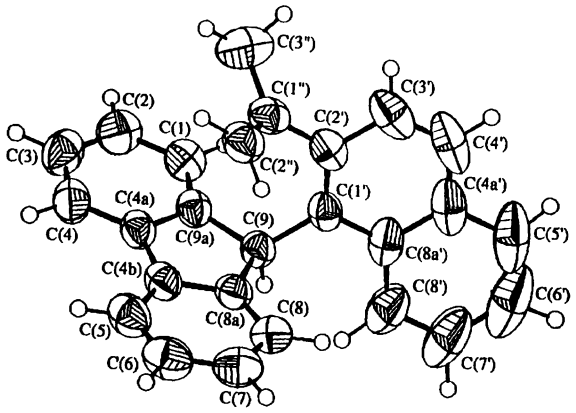


Fig. 1. An ORTEP drawing of compound *sp*-**2**.

olefinic carbon is a little closer to the fluorene ring than the methyl carbon (Table 4) and is located above the carbon atoms 8a and 8. This is probably because the methyl group is bulkier than a π-system. Indeed, the methyl group, which is located closely to C(1), is bent away from the fluorene ring by 0.10 Å from the plane, which is made by C(2′)–C(1″)–C(2″), to save the repulsion energy. The distance between the average plane of the ethenyl group and that of the fluorene ring is ca. 3 Å and that between the C(1″) of the side chain and the nearest carbon, C(9), of the fluorene ring is 3.0 Å. These results explain the easy formation of the ring compound **10**. The naphthyl group does not eclipse the 9-C–H bond but forms a dihedral angle of 17.2° (Table 3) in agreement with the MMP2 result (ca. 15°). Thus the molecule is chiral.

There are no abnormal bond lengths in the molecule. Although angles C(8a)–C(9)–C(1′) and C(9a)–C(9)–C(1′) are unusually large (Table 2), 115.7 and 119.0°, respectively, these are to avoid severe steric interferences between the naphthyl group and the fluorene moiety and are commonly seen in other molecules of this type.[10] As are seen in Table 2, some deviations from the normal bond angles were also observed at the carbon atoms connecting the olefinic side chain.

Table 4. Selected Nonbonding Distances in Compound *sp*-**2**

Atom–Atom	Distance/Å	Atom–Atom	Distance/Å
C(1″)–C(1)	3.488	C(2″)–C(8)	3.388
C(1″)–C(2)	4.311	C(2″)–C(8a)	3.219
C(1″)–C(9)	3.025	C(2″)–C(9a)	3.444
C(1″)–C(9a)	3.027	C(3″)–C(1)	3.432
C(2″)–C(1)	4.229	C(3″)–C(2)	3.920
C(2″)–C(4a)	3.567	C(3″)–C(9a)	3.538
C(2″)–C(4b)	3.344		

Structure of Cyclized Product 10. Knowing the structures of the starting olefins, we were interested in knowing the structure of the cyclic product (**10**) in more detail. An NOE experiment between the protons of 8-methyl group and the 14c-H showed 18% enhancement of the signal intensity, whereas that between the protons of the bromomethyl group and the 14c-H only 4%. This indicates that the methyl group and 14c-H are close and supports the *cis*-structure for the methyl and the hydrogen.

Confirmation of the structure of **10** was made by X-ray crystallography. Atomic coordinates and an ORTEP drawing with numbering of carbon atoms are given in Table 5 and Fig. 2, respectively. The relative configuration is the same as predicted by the NOE experiment. The methyl group at the 8-position is cis and the bromomethyl group is trans to the 14c hydrogen. The conformation of the cyclohexadiene ring is a distorted shallow boat form, in which C(8) and C(14c) are bows, as are in other cases.[11] The torsion angles, C(14c)–C(14e)–C(7a)–C(8) and C(14c)–C(14b)–C(8a)–C(8), are 4.2° and 14.8°, respectively. The methyl group at the 8-position, C(16), and 14c-H are close with each other: The distance between the carbon of the methyl and 14c-H is 3.02 Å. The large NOE observed for the methyl and the 14c-H is well accounted for by the structure. The strain caused by forming the ring is mainly relieved by bond angle deformations. Bond lengths in the molecule are nearly normal, if not completely so. However, there

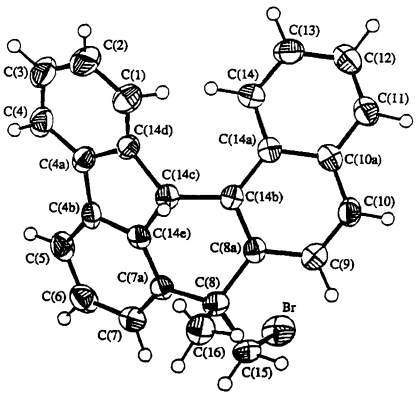


Fig. 2. An ORTEP drawing of compound **10**.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters with Estimated Standard Deviations in Parentheses for ($8R^*$,14cS^*)-8-Bromomethyl-8-methyl-8,14c-dihydrodibenz[a,l]aceanthrylene (**10**)

Atom	x	y	z	B_{eq}
C(1)	5814(1)	−1243(2)	1062(1)	5.8(1)
C(2)	5173(1)	−1388(2)	1716(2)	6.6(1)
C(3)	4153(1)	−816(2)	2178(2)	6.4(1)
C(4)	4939(1)	−80(1)	1976(2)	5.4(1)
C(4a)	5582.2(9)	73(1)	1320(2)	4.42(9)
C(4b)	5895.4(9)	784(1)	926(1)	4.20(9)
C(5)	5708(1)	1524(1)	1135(2)	5.04(9)
C(6)	6160(1)	2077(1)	656(2)	5.5(1)
C(7)	6788(1)	1905(1)	−15(2)	4.97(9)
C(7a)	6978(1)	1164(1)	−235(1)	4.07(9)
C(8)	7641.0(9)	873(1)	−946(1)	4.08(9)
C(8a)	7969.3(9)	166(1)	−390(1)	3.98(9)
C(9)	8741(1)	−18(1)	−580(2)	4.67(9)
C(10)	9080(1)	−604(1)	−57(2)	4.9(1)
C(10a)	8680.6(9)	−1019.2(9)	764(2)	4.32(9)
C(11)	9058(1)	−1558(1)	1440(2)	5.0(1)
C(12)	8694(1)	−1912(1)	2299(2)	5.6(1)
C(13)	7929(1)	−1745(1)	2534(2)	5.4(1)
C(14)	7540(1)	−1240(1)	1867(2)	4.67(9)
C(14a)	7892.4(9)	−870.5(9)	949(1)	4.02(9)
C(14b)	7526(1)	−310.6(9)	272(1)	3.84(9)
C(14c)	6666(1)	−192(1)	152(1)	4.09(9)
C(14d)	6033(1)	−509(1)	902(2)	4.49(9)
C(14e)	6516.1(9)	627(1)	240(1)	3.85(9)
C(15)	8242(1)	1475(1)	−1143(2)	4.75(9)
C(16)	7351(1)	686(1)	−2166(2)	5.2(1)
Br	8783.3(1)	1784.1(1)	227.2(2)	5.69(8)

are some abnormal bond angles, as are seen in Table 6. Bond angles involving C(14d) seem abnormal but they are normal for fluorene compounds, whereas those involving C(14e) seem normal but they are significantly different from the angles observed for C(14d). Angles involving C(14c) are strikingly different from the normal tetrahedral angle.

Dynamics of *sp*-2. Although the structure of *sp*-**2** in crystals is established, it does not mean that the structure is as such in solutions. Indeed, ^{1}H NMR spectra recorded at various temperatures indicate that there is dynamics of molecules. In order to get further insight, we performed dynamic NMR study of *sp*-**2**. Before doing so, however, it was necessary to assign all the protons because the NMR spectra showed that there were protons that did not exchange their sites, although many of protons did so. The assignment was possible through a COSY spectrum and NOE experiments. It showed that the protons that exchange their sites all belong to the fluorene moiety but those which belong to the naphthalene ring and the side chain did not exchange their sites. The 9-H proton of the fluorene ring also did not show change in its line-shape. Although it is possible to argue that the observed dynamics is the isomerization between **13** and **14**, it does not explain

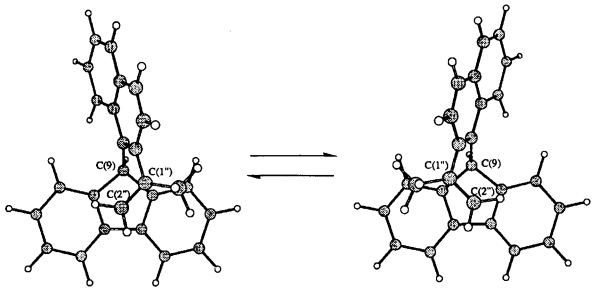
Table 6. Selected Bond Angles in Compound **10**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(7)	C(7a)	C(8)	127.6(2)	C(8a)	C(14b)	C(14a)	119.2(2)
C(7)	C(7a)	C(14e)	116.6(2)	C(8a)	C(14b)	C(14c)	114.5(1)
C(8)	C(7a)	C(14e)	115.8(2)	C(14a)	C(14b)	C(14c)	126.2(1)
C(7a)	C(8)	C(8a)	109.5(1)	C(14b)	C(14c)	C(14d)	127.9(1)
C(7a)	C(8)	C(15)	111.7(1)	C(14b)	C(14c)	C(14e)	107.6(1)
C(7a)	C(8)	C(16)	109.2(1)	C(14d)	C(14c)	C(14e)	101.3(1)
C(8a)	C(8)	C(15)	112.8(1)	C(1)	C(14d)	C(4a)	120.2(2)
C(8a)	C(8)	C(16)	109.7(2)	C(1)	C(14d)	C(14c)	129.3(2)
C(15)	C(8)	C(16)	103.8(1)	C(9)	C(14d)	C(14c)	109.8(2)
C(8)	C(8a)	C(9)	119.0(1)	C(4b)	C(14e)	C(7a)	124.0(2)
C(8)	C(8a)	C(14b)	122.2(1)	C(4b)	C(14e)	C(14c)	112.2(1)
C(9)	C(8a)	C(14b)	118.2(2)	C(7a)	C(14e)	C(14c)	123.6(1)

the observed line-shape change because, if it were the case, the protons belonging to the side chain as well as the 9-H should have changed their chemical shifts. The only possible way of explaining the observed changes in line-shapes is racemization of conformation **13**. The process may be depicted by the following scheme, which uses the MMP2 structures (Scheme 1). This is the first example of a gearing motion of two-two-toothed gears and adds a further example to the molecular gear in addition to two-three-toothed[12] and three-three-toothed gears.[13]

The activation energy for the racemization was difficult to obtain from ^{1}H NMR spectra because of heavy overlaps in aromatic proton regions, where line-shape change took place. Thus we decided to perform kinetics by ^{13}C dynamic NMR. ^{13}C signals of the aromatic region could be assigned, except those which did not carry a proton, through a H–C COSY spectrum. The signals due to C(4)/C(5) were found to be convenient for the analysis. The line shape analysis of these signals afforded the following activation parameters: $\Delta H^{\ddagger}=8.8\pm0.5$ kcal mol^{-1}, $\Delta S^{\ddagger}=-9\pm2$ cal mol^{-1} K^{-1}, $\Delta G^{\ddagger}_{233}=10.9$ kcal mol^{-1} (dichloromethane-d_2 solvent). Free energies of activation for the isomerization were also obtained to be 10.9—11.0 kcal mol^{-1} by using other pairs of carbon signals by the coalescence temperature technique.[14]

Mechanisms of the Reactions. Coming back to the addition of bromine to *sp*-**2**, we can now discuss the



Scheme 1. Observed dynamics (racemization) in compound *sp*-**2**.

mechanisms in more detail. Since the molecule exists as conformation **13** or its enantiomer in solution and we do not distinguish enantiomers, discussion on the reaction of conformation **13** suffices. When a bromine cation adds to *sp*-**2**, it will form the intermediate **11**. In this intermediate, the bromine bridge[15,16] that is seen in addition of bromine to an olefinic bond will not exist for the following two reasons.[17] Firstly, if such a bridged bromonium ion is formed, the carbon directly connected to the naphthyl group must assume sp^3 hybridization, which is too unstable because of the steric effect. Secondly, the open carbenium ion is stabilized by the π-participation because the π-system is well in proximity. The open cation **11** should be vulnerable to the attack of an existing anion to deprotonate and to the attack of the fluorene ring. These explain the formation of compounds *ap*-**8**, *ap*-**9**, and **10**. The exclusive formation of **10** without formation of its stereoisomer may be rationalized in the following way. When *sp*-**2** reacts with a bromine cation, it forms cation **11** which reacts with the fluorene ring before rotating. The barrier to rotation of this moiety should be higher than that in compound *sp*-**2** because the side chain is more bulky in the cation than in *sp*-**2** and the cation is stabilized by π-participation.

We have invoked a bridged bromonium ion in the case of *ap*-**2** and wrote a structure as **12**. There are several reasons for writing such a structure. Although the presence of an aromatic ring shifts an equilibrium between a bridged bromonium ion and an open β-bromo-cation species to the open cation,[18] and it is more so when a methyl group is present,[19,20] because the ethenyl group in *ap*-**2** is not coplanar with the naphthyl group. Since unbridging in the bromonium cation owes to the stabilization of a classical cation which is largely due to conjugation with the aryl group, the nonplanarity should enhance the bridged nature of the cation. Formation of the bromine adduct *sp*-**7** from *ap*-**2** as a sole product also supports this argument.

Ionization of *sp*-7 and Related Compound. The foregoing discussion necessitates comparison of the properties of *sp* and *ap* cations (**11** and **12**) produced from the olefin **2** and bromine cation. Thus we performed ionization of *sp*-**7** with silver *p*-toluenesulfonate. This salt was selected because proton affinity of *p*-toluenesulfonate anion is close to that of bromide anion[21] and nucleophilicity of the former is rather low.

The reaction of *sp*-**7** with silver *p*-toluenesulfonate in dichloromethane at room temperature afforded *sp*-2-[(*E*)-2-bromo-1-methylethenyl]-1-(9-fluorenyl)naphthalene (*sp*-**9**) and *sp*-2-[1-(bromomethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*sp*-**8**) in 1 : 9 ratio but no cyclized product was observed (Chart 6). The absence of the last compound is consistent with other observations[22] and is due to the fact that the cation produced in the vicinity of 9-H is in the plane of the fluorene ring and is not capable of attacking the π-system of the fluorene.

For comparison, addition of bromine to *sp*-**2** was also carried out in dichloromethane solvent. The product ratios were *ap*-**8** : *ap*-**9** : **10**=25 : 60 : 15. If we exclude the cyclized compound **10**, the ratio of the bromo-olefin to the bromomethyl-olefin shows that the latter is the main product in this case. They are very different indeed.

That the products *sp*- and *ap*-**8** as well as *sp*- and *ap*-**9** are pairs of rotational isomers with each other was proved by heating them in toluene. The *sp*/*ap* ratios were 9 and 2.4, respectively, for **8** and **9** in toluene-d_8 at 110°C. In each case, the *ap* isomer that possesses the side chain upon the fluorene ring is less stable, in agreement with the parent compound **2**, but the ratios seem to be affected by the substituent.

The difference in the formation ratios of bromo-olefins **8** and **9** in *sp* and *ap* forms may be again attributed to the difference in the degree of openness of the bromonium ion. Treatment of (1,2-dibromo-1-methylethyl)benzene (**15**) with silver *p*-toluenesulfonate afforded 77 : 23 the bromomethyl-olefin (**16**) and the bromo-olefin (**17**) (Chart 7). This ratio is inbetween the result obtained for bromine addition to *sp*-**2** and that for the treatment of *sp*-**7** with silver *p*-toluenesulfonate. In the cation formed from **15**, the cationic and the aromatic ring must be close to coplanar conformation and bridging is known to be weak, though there is contribution of bridging.[19] In cation **12**, we postulate that bromine bridging is almost complete, because the cation plane cannot be coplanar with the naphthyl ring. In contrast, the cation **11** is almost completely open. The product ratios imply that the more open is the 3-membered bromonium ion ring, the less produced the bromomethyl compound.

Experimental

^1H and ^{13}C NMR spectra were obtained on a JEOL GSX-400 machine operating at 400 MHz and 100 MHz, respectively. NOE experiments were carried out by degassed solutions of chloroform-*d* at room temperature. Irradiation time and power were 5 s and IRA=350, respectively, and a 45° pulse was used. DEPT and C–H COSY spectra were measured on a Varian Gemini-300. Mass spectra were measured

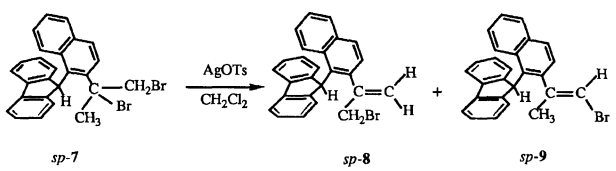


Chart 6.

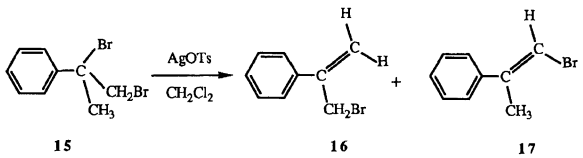


Chart 7.

on a JEOL JMS-DX303 spectrometer. Elemental analyses were performed by a Pekin-Elmer 240C analyzer. UV spectra were measured on a Hitachi U-2000 spectrometer. Melting points are not corrected. *sp*-1-(9-Fluorenyl)-2-naphthoic acid (**4**) was obtained by the method published[8] and was converted to the corresponding methyl ester (**5**).[4]

2-[*sp*-1-(9-Fluorenyl)-2-naphthyl]-2-propanol (6). To a Grignard solution prepared from 1.82 g (75 mmol) of magnesium, 10.6 g (75 mmol) of iodomethane, and 80 mL of ether, was added 10.5 g (30 mmol) of the methyl ester (**5**) in 30 mL of tetrahydrofuran. The mixture was heated under reflux for 1 h and decomposed with aqueous ammonium chloride. The solvent was evaporated and the residue was chromatographed on silica gel with 1 : 1 hexane-dichloromethane eluent. Yield 5.78 g (55%), mp 175—179°C. The reported mp is 133—134°C.[4] ^{1}H NMR ($CDCl_3$) δ=1.99 (6H, s), 2.02 (1H, s), 6.45 (1H, d, J=8.6 Hz), 6.78 (1H, ddd, J=8.6, 6.5, and 1.4 Hz), 6.85 (1H, s), 7.11—7.22 (5H, m), 7.40 (2H, t, J=7.4 Hz), 7.69 (1H, d, J=7.5 Hz), 7.77 and 7.79 (2H, ABq, J=8.9 Hz), 7.96 (2H, d, J=7.9 Hz).

***ap*-1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene (*ap*-2).** A mixture of 5.78 g (16 mmol) of the alcohol (**6**), 2.96 g (37 mmol) of pyridine, and 7.12 g (37 mmol) of *p*-toluenesulfonic acid monohydrate in 300 mL of toluene was heated under reflux, with a Dean-Stark apparatus attached to the flask, for 12 h. The conversion was checked by TLC. The mixture was then washed with water and the solvent was evaporated. The residue was chromatographed on silica gel with hexane eluent. It was obtained in 4.28 g (78%) yield. The analytical sample was purified by recrystallization from hexane-dichloromethane, mp 149.5—150.5°C. Found: C, 93.85; H, 6.11%. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06%. ^{1}H NMR ($CDCl_3$) δ=2.31 (3H, t, J=1.2 Hz), 5.23 (1H, app q, J=1.2 Hz), 5.37 (1H, app quintet, J=1.7 Hz), 5.86 (1H, s), 6.42 (1H, dd, J=8.6 and 0.7 Hz), 6.83 (1H, ddd, J=8.6, 6.8, and 1.4 Hz), 7.12—7.23 (5H, m), 7.40 (2H, m), 7.43 (1H, d, J=8.4 Hz), 7.71 (1H, d, J=7.9 Hz), 7.77 (1H, d, J=8.6 Hz), 7.94 (2H, d, J=7.5 Hz). ^{13}C NMR ($CDCl_3$) δ=26.4, 51.2, 115.9, 120.3, 124.1, 125.0, 125.5, 125.8, 126.1, 126.9, 127.3, 127.9, 128.2, 131.4, 133.5, 140.1, 144.4, 146.8, 148.9. UV absorptions (hexane solvent, log ε is given in parentheses) 211.6 (4.81), 226.4 (4.83), 266.4 (4.32), 289.4 (4.07), 300.4 (4.02), 314.4 (sh 2.50) nm.

***sp*-1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene (*sp*-2).** To a solution of 2.00 g (6.0 mmol) of the *ap* form in 60 mL of 1,2-dimethoxyethane cooled at −20—−30°C, was added 10.0 mL (15.6 mmol or 2.6 equiv) of 15% butyllithium in hexane under a nitrogen atmosphere. The mixture was allowed to warm up to the room temperature and then heated under reflux for 2 h. The cooled mixture was poured into water which contained 10 equiv of acetic acid with ice-cooling. The organic materials were extracted with dichloromethane and dried. After evaporation of the solvent, the residue, which consisted of ca. 1 : 1 *ap* and *sp* isomers, was submitted to chromatography on silica gel with hexane eluent. The *sp* isomer was eluted first and then the *ap* isomer. The *sp* isomer was purified by recrystallization from dichloromethane-hexane, mp 157.5—158.0°C. Found: C, 94.06; H, 6.03%. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06%. ^{1}H NMR ($CDCl_3$) δ=1.33 (3H, t, J=1.2 Hz, CH_3), 3.48 (1H, app q, J=1.0 Hz, vinyl proton cis to naphthyl), 4.05 (1H, app quintet, J=1.5 Hz, vinyl proton trans to naphthyl), 6.05 (1H, s, 9-H), 7.11 (1H, d, J=8.6 Hz, 3′-H), 7.19 (2H, dt, J=7.5 and 1.0 Hz, 2,7-H), 7.23 (2H, app d, J=7.2 Hz, 1,8-H), 7.37 (2H, app t, J=7.2 Hz, 3, 6-H), 7.57 (1H, ddd, J=8.2, 6.8, and 1.4 Hz, 6′-H), 7.66 (1H, ddd, J=8.6, 6.8, and 1.4 Hz, 7′-H), 7.78 (1H, d, J=8.6 Hz, 4′-H), 7.79 (2H, dd, J=7.5 and 1.0 Hz, 4,5-H), 7.94 (1H, dd, J=7.9 and 1.4 Hz, 5′-H), 8.59 (1H, dd, J=8.9 and 1.4 Hz, 8′-H). All proton signals were assigned by proton decoupling and NOE experiments. ^{13}C NMR ($CDCl_3$, r.t.) δ=23.3 (q, CH_3), 48.3 (d, 9-C), 115.7 (t, methylene), 119.9 (d, 4,5-C), 124.0 (d, 8′-C), 124.5 (d, 1,8-C), 125.3 (d, 6′-C), 126.7 (three signals overlapped, 2,7-C, 3,6-C, 7′-C), 127.1 (d, 4′-C), 127.7 (d, 3′-C), 128.9 (d, 5′-C), 132.2 (s), 133.0 (s), 134.4 (s), 141.2 (2), 142.2 (s), 142.7 (s) 149.0 (s). Number of attached protons was determined by a DEPT experiment and all carbon atoms that carried proton(s) were assigned by a C–H COSY spectrum. (CD_2Cl_2, −80°C) δ=23.0, 47.6, 114.8, 119.3, 120.2, 123.6, 123.8, 124.3, 125.1, 126.2, 126.3, 126.4, 126.7, 126.8, 128.4, 131.9, 132.2, 133.8, 139.5, 141.1, 141.3, 142.5, 146.9, 150.2. UV absorptions (hexane solvent, log ε is given in parentheses) 207.2 (4.71), 228.4 (4.70), 269.4 (4.20), 291.2 (4.00), 303.0 (3.97), 320.6 (sh 2.51) nm.

Reaction of *sp*-2 with Bromine in Carbon Tetrachloride. To a solution of 170 mg (0.51 mmol) of the olefin in 10 mL of carbon tetrachloride, was gradually added a solution of 81.7 mg (0.51 mmol) of bromine in 3 mL of carbon tetrachloride at room temperature. The color of the solution faded immediately after the addition and a copious amount of hydrogen bromide was evolved. After the completion of addition of bromine, the mixture was stirred for 2 h to confirm the completion of the reaction and the mixture was washed with aqueous sodium hydrogencarbonate. The solvent was evaporated and ^{1}H NMR spectra were taken. The spectrum at 400 MHz indicated that it was a 30 : 58 : 12 mixture of bromo-olefin, bromomethyl compound, and the cyclized compound. The characterization of these compounds are given below. Chromatography on silica gel using hexane-to-1 : 1 mixture of hexane-dichloromethane afforded three products. The combined yields of these compounds were almost quantitative.

Fraction 1 afforded a product, mp 142.0—143.0°C, which showed the following ^{1}H NMR spectrum ($CDCl_3$) δ=1.27 (3H, d, J=1.4 Hz), 4.58 (1H, app d, J=1.4 Hz), 6.00 (1H, s), 7.02 (1H, d, J=8.6 Hz), 7.14—7.26 (4H, m), 7.38 (2H, t, J=7.7 Hz), 7.58 (1H, app t, J=7.4 Hz), 7.67 (1H, ddd, J=8.6, 6.8, and 1.4 Hz), 7.76 (1H, d, J=8.6 Hz), 7.87 (2H, d, J=7.5 Hz), 7.93 (1H, dd, J=7.9 and 1.0 Hz), 8.58 (1H, d, J=8.9 Hz). Found: C, 75.62; H, 4.74%. Calcd for $C_{26}H_{19}Br$: C, 75.92; H, 4.66%. This compound was identified as *ap*-2-[(*E*)-2-bromo-1-methylethenyl]-1-(9-fluorenyl)naphthalene (*ap*-**9**), by the data given above as well as by the isomerization experiments. When the signal due to the methyl protons (δ=1.27) was irradiated, 9-H (δ=6.00) and some of the aromatic proton signals increased in their intensities (less than 2%).

Fraction 2 afforded a product, mp 116—122°C (decomp), which showed the following ^{1}H NMR spectral data ($CDCl_3$) δ=3.12 (2H, app d, J=0.7 Hz), 3.95 (1H, app d, J=0.7 Hz), 4.64 (1H, app d, J=0.7 Hz), 6.09 (1H, s), 7.18—7.23 (4H, m), 7.34 (1H, d, J=8.6 Hz), 7.38 (2H, m), 7.60 (1H, ddd, J=7.9, 6.8, and 1.0 Hz), 7.68 (1H, ddd, J=8.2, 6.8, and 1.4 Hz), 7.79 (2H, d, J=7.5 Hz), 7.80 (1H, d, J=8.6 Hz), 7.96

(1H, d, J=7.9 Hz), 8.60 (1H, d, J=8.6 Hz). High resolution MS: M^+, 410.0611. Calcd for $C_{26}H_{19}{}^{79}Br$: M, 410.0670. This compound was identified as *ap*-2-[1-(bromomethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*ap*-**8**) by the spectral data as well as the isomerization experiments.

Fraction 3 afforded a product, decomposition point 166—173°C, which showed the following ^{1}H NMR data ($CDCl_3$) δ=1.75 (3H, s), 4.41 (2H, ABq, J=10 Hz, $\Delta\nu$=5 Hz), 5.38 (1H, s), 7.37—7.54 (6H, m), 7.67 and 7.73 (2H, ABq, J=8.9 Hz), 7.84—7.90 (3H, m), 8.10 (1H, d, J=7.9 Hz), 8.75 (1H, d, J=8.6 Hz). Found: C, 75.69; H, 4.50%. Calcd for $C_{26}H_{19}Br$: C, 75.92; H, 4.66%. High resolution MS: M^+, 410.0642. $C_{26}H_{19}{}^{79}Br$ requires 410.0670. When the signal (δ=1.75) due to the methyl protons was irradiated, 9-H (δ=5.38) and bromomethyl (δ=4.41) signals were enhanced by 18% and 4%, respectively. This compound was identified as (8R^*,14cS^*)-8-bromomethyl-8-methyl-8,14c-dihydrodibenz[*a*,*l*]aceanthrylene (**10**).

Reaction of *sp*-2 with Bromine in Dichloromethane. The reaction was carried out similarly as for the carbon tetrachloride case. The formation ratio of *ap*-**8**, *ap*-**9**, and **10** was 25 : 60 : 15, as was detected by ^{1}H NMR spectra.

Bromination of *ap*-Olefin (*ap*-2). The bromination was carried out as described in the bromination of the *sp*-isomer. The feature of the reaction was very slow fading of the bromine color. After two hour stirring, the mixture was treated similarly. *sp*-2-(1,2-Dibromo-1-methylethyl)-1-(9-fluorenyl)naphthalene (*sp*-**7**), mp 157.0—158.0°C, was obtained in 90% yield. This compound failed to give correct analysis but gave the following spectral data, which showed absence of impurities. High resolution MS; M^+, 489.9930. Calcd for $C_{26}H_{20}{}^{79}Br_2$: M, 489.9932. Low MS (relative intensity given in parentheses) 494 (0.48), 492 (1.0), 490 (0.50). ^{1}H NMR ($CDCl_3$) δ=2.74 (3H, s), 4.29 and 4.92 (2H, ABq, J=10.3 Hz), 6.49 (1H, d, J=8.9 Hz), 6.71 (1H, s), 6.80 (1H, ddd, J=8.9, 6.8, and 1.4 Hz), 7.15—7.26 (4H, m), 7.38—7.47 (3H, m), 7.71 (1H, d, J=7.9 Hz), 7.78 and 7.89 (2H, ABq, J=9.2 Hz), 7.94—8.01 (2H, m).

Treatment of Compound *sp*-7 with Silver *p*-Toluenesulfonate. To a solution of 136 mg (0.28 mmol) of the dibromide in 30 mL of dichloromethane was added 85 mg (0.30 mmol) of silver *p*-toluenesulfonate and the mixture was stirred for 1 h at room temperature. The mixture was poured into aqueous sodium hydrogencarbonate and extracted with dichloromethane. The solvent was evaporated from the extract and the residue was submitted to chromatography on silica gel with hexane eluent. TLC showed the presence of two compounds and the ratio was 9 : 1 in favor of the less easily eluted.

Fraction 1 afforded a crystalline compound which was recrystallized from dichloromethane-hexane, mp 170.0—171.5°C. This compound was identified as *sp*-2-[(*E*)-2-bromo-1-methylethenyl]-1-(9-fluorenyl)naphthalene (*sp*-**9**). Found: C, 75.76; H, 4.63%. Calcd for $C_{26}H_{19}Br$: C, 75.92; H, 4.66%. ^{1}H NMR ($CDCl_3$) δ=2.39 (3H, d, J=1.4 Hz), 5.63 (1H, s), 6.43 (1H, d, J=8.6 Hz), 6.47 (1H, q, J=1.4 Hz), 6.85 (1H, ddd, J=8.6, 7.2, and 1.4 Hz), 7.11 (2H, d, J=7.5 Hz), 7.16—7.27 (3H, m), 7.38 (1H, d, J=8.6 Hz), 7.42 (2H, t, J=7.5 Hz), 7.72 (1H, d, J=8.2 Hz), 7.79 (1H, d, J=8.6 Hz), 7.95 (2H, d, J=7.5 Hz).

The second fraction gave also a crystalline compound which was recrystallized from dichloromethane-hexane, mp 137.0—138.0°C. This compound was identified as *sp*-2-[1-(bromomethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*sp*-**8**). Found: C, 70.26; H, 4.40%: Calcd for $C_{26}H_{19}Br\cdot(CH_2Cl_2)_{1/2}$: C, 70.14; H, 4.44%. ^{1}H NMR ($CDCl_3$) detected the presence of the dichloromethane in crystals: δ=4.48 (2H, app d, J=0.7 Hz), 5.56 (1H, app d, J=1.0 Hz), 5.77 (1H, s), 5.78 (1H, app d, J=1.0 Hz), 6.45 (1H, d, J=8.9 Hz), 6.85 (1H, ddd, J=8.6, 7.2 and 1.4 Hz), 7.16—7.26 (5H, m), 7.38—7.45 (2H, m), 7.47 (1H, d, J=8.6 Hz), 7.74 (1H, d, J=7.9 Hz), 7.81 (1H, d, J=8.6 Hz), 7.94 (2H, d, J=7.5 Hz).

Treatment of (1,2-Dibromo-1-methylethyl)benzene (15) with Silver *p*-Toluenesulfonate. The reaction was carried out similarly as mentioned above. The products were identified by ^{1}H NMR spectra by comparing with those of 1-bromomethylethenylbenzene (**16**)[23] and [(*E*)-2-bromo-1-methylethenyl]benzene (**17**)[24] which were prepared by the methods in the literature.

Isomerization of Rotamers of Bromoolefins. A solution of ca. 10 mg of a substrate in ca. 0.5 mL of toluene-d_8 was heated at 100°C for 6 h. This isomerization was carried out for each rotamer of the two olefins. Both pairs of isomers gave identical NMR spectra at the end of heating. The *sp*/*ap* ratios for the bromo-olefin and the bromomethylolefin were 7 : 3 and 9 : 1, respectively.

Kinetics of Isomerization. A solution of 15.0 mg of *sp*-**2** containing ca. 4% *ap*-**2** in 0.60 mL of toluene-d_8 was heated in a boiling benzene bath (80.5°C). The increase in the amount of *ap*-**2** and the decrease in *sp*-**2** were recorded by ^{1}H NMR spectra at appropriate intervals. The population ratio, *ap*/*sp*, at 80.5°C was 15.6 at equilibrium. The following [*ap*]/[*sp*] ratios were obtained (time/s in parentheses): 0.039 (0), 0.22 (1800), 0.40 (3600), 0.96 (7200), 1.7 (10800), 2.6 (14400), 5.1 (21600). These ratios were used for calculation of the rate constants, assuming the reversible first order reaction. The rate constant at the temperature was obtained as $(7.7\pm0.5)\times10^{-5}$ s^{-1}. The free energy of activation at the temperature is 27.5 kcal mol^{-1}.

Dynamic NMR Measurements. A dichloromethane-d_2 solution (0.6 mL) of the *sp*-olefin (50 mg) was used for ^{1}H and ^{13}C NMR measurements at various temperatures, which were calibrated by methanol signals. The data were accumulated more than 200 times for ^{13}C measurements. The lineshape analyses were performed by DNMR3K program.[25] The carbon signals due to the fluorene moiety (δ=119.9 at r.t.) were used for the analyses. The chemical shift differences ($\Delta\nu$) and T_2 values were determined from the spectra observed at several temperatures where the exchanges were negligibly slow. These parameters and rate constants are as follows: $\Delta\nu$=88.0 Hz, T_2=0.13—0.16 s, rate constants k/s^{-1} (temperature/°C in parentheses) 40 (−60.8), 70 (−55.3), 105 (−50.1), 150 (−47.1), 175 (−45.1), 280 (−40.0), 430 (−35.2). These rate constants afforded the following parameters by putting them into the Eyring equation: $\Delta H^{\ddagger}$=8.8±0.5 kcal mol^{-1}, $\Delta S^{\ddagger}$=−9±2 cal mol^{-1} K^{-1}, $\Delta G^{\ddagger}_{233}$=10.9 kcal mol^{-1}. The free energies of activation were also determined by the coalescence method by using three other signals at 124.5, 141.2, and 149.0 ppm at room temperature. Chemical shift differences, coalescence temperatures, and free energies of activation at the coalescence temperatures follow: δ=124.5, 67.5 Hz, −47.2°C, 10.9 kcal mol^{-1}; δ=141.2, 167.3 Hz, −38.3°C, 10.9 kcal mol^{-1}; δ=149.0,

Table 7. Crystal and Structure Analysis Data of Compounds *sp*-**2** and **10**

Compound	*sp*-**2**	**10**
Formula	$C_{26}H_{20}$	$C_{26}H_{19}Br$
F. W.	332.40	411.30
Crystal size/mm^3	0.35×0.30×0.20	0.50×0.35×0.20
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pcab$
a/Å	13.519(3)	17.588(3)
b/Å	11.373(2)	17.935(3)
c/Å	13.419(4)	17.773(3)
β/°	114.25(2)	90
V/Å^3	1843.3(7)	3714(1)
Z	4	8
D_c/g cm^{-3}	1.20	1.47
μ/cm^{-1}	4.39	28.36
2θ range/°	3—130	3—130
No. of data	3488	3592
No. of data used	2849	2979
R	0.053	0.036
R_w	0.065	0.060

310.8 Hz, −29.3°C, 11.0 kcal mol^{-1}.

MM2 Calculations. Calculations were performed on an NEC RA-9800 computer by using the MM2(85) program. Force field parameters were used without modifications. Planar π-systems were used for conjugated systems.

X-Ray Analyses.[27] Crystals suitable for X-ray crystallography were grown from hexane and acetonitrile for compounds *sp*-**2** and **10**, respectively. X-Ray data were obtained on a MAC Science MXC18 four-circle diffractometer with Cu $K\alpha$ radiation (λ=1.54178 Å). The scan mode was the ω-2θ method in all range. The scan rate was 10° min^{-1} and the scan range was calculated by A+0.35° tanθ, where A's were 1.55° and 1.51° for compounds *sp*-**2** and **10**, respectively. The structures were solved by the direct method (MITHRIL 91) and refined by the full-matrix least-squares method using the CRYSTAN program on an NSSUN work-station. Anisotropic thermal parameters were employed for nonhydrogen atoms and isotropic for hydrogens. No absorption correction was made for *sp*-**2**, whereas analytical absorption correction was applied for **10**. The reflections with $|F_o|>3\sigma|F_o|$ were used for the structure determination and refinement and the function minimized was $\sum[w(|F_o|^2-|F_c|^2)^2]$, in which $w=[(\sigma_c|F_o|)^2+0.0004|F_o|^2]^{-1}$. Additional experimental data are given in Table 7.

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