Hindered Rotation in Diphenylmethane Derivatives. Electrostatic vs Charge-Transfer and Homoconjugative Aryl−Aryl Interactions

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Abstract: A series of *p*,*p*′-disubstituted 7-phenyl-7-(2-fluorophenyl)norbornanes **5xy** has been prepared, and the barrier ($\Delta G^{\#}$) to 160° libration around the 2-fluoroaryl-norbornane bond has been measured by DNMR. There is spectroscopic evidence of strong homoconjugative and charge-transfer (CT) interactions between both aryl groups of **5xy**. However, the relationship between $\Delta G^{\#}$ and the nature of the substituents X and Y is accounted for only by electrostatic interactions between both aryl groups in the ground state as well as in the transition state of the libration. Therefore, the notion of CT and aromatic homoconjugation as strong attractive forces between aryl groups should be definitively rejected.

Introduction

Noncovalent interactions between aromatic molecules play a fundamental role in determining the structure of molecular assemblies in biology, chemistry, and material sciences.[1] The interactions between aromatic molecules include charge-transfer (CT), dispersive, and electrostatic components.[1a] However, the relative significance of these factors is not well understood. Recent experimental work shows that the arene−arene interactions in the case of substituted 1,8-diarylnaphthalenes, whose aryl groups are arranged in a face-to-face stacked geometry, are dominated by electrostatic interactions between the aryl groups in the ground state.[2] However, this substrate is not adequate for the study of the relevance of CT effects because no CT band is observed in the UV spectrum.[2a]

The 7,7-diarylnorbornane system (Scheme 1) is an interesting substrate to gain further knowledge of noncovalent as well as homoconjugative interactions between aromatic molecules. The aryl groups of the more stable conformation of 7,7-diphenylnorbornane (**6**)[3] adopt a peculiar face-to-face arrangement, which can be designed as apical homoconjugated. In contrast with this, the disposition in triptycenes and related compounds can be named lateral homoconjugated. The aryl rings of diphenylmethane are arranged nearly orthogonally and do not show conformational stability (propeller compounds).[4] The adoption of the apical cofacial disposition in the case of **6** is forced by the steric effect of the four *exo*-norbornylic C−H bonds. A related conformation is shown by a bis(*p*-bromophenyl)-fulleroid[5a] and some 1,1-diphenylcyclopropane derivatives.[5b,c]

The X-ray measured $C_{ipso}-C_{ipso}$ distance (2.46 Å)[3] of **6** is even shorter than the $C_{ipso}-C_{ipso}$ distance of the 1,8-diarylnaphthalene system (2.8 Å)[2a] and should favor any CT and homoconjugative effects over electrostatics. Thus, the distance dependence of electrostatic interactions between π systems ranges from r^{-1} to r^{-5}, whereas orbital interaction varies with e^{-r}.[6] As shown by the crystal structure analysis of **6**, there is no warping of the aromatic rings.

Results

Preparation of 7,7-Diphenylnorbornanes 5. We have synthesized the series of 7,7-diarylnorbornanes **5aa**, **5ca**, **5ac**, **5da**, **5dc**, **5ec**, and **5cc** by successive coupling of the two aryl units starting from 7-norbornanone (**1**), according to Scheme 1. This procedure is more versatile than the uncatalyzed Friedel−Crafts reaction of 7,7-bis(triflyloxy)norbornane with benzene derivatives, our first approach to the 7,7-diphenylnorbornane system.[3]

The nitrile **5fc** was prepared by reaction of the bromo derivative **5ec** with KCN, catalyzed by Ni(0)[7] (Scheme 1). The nitro compounds **5ga** and **5ag** were synthesized by nitration of **5aa** with $NaNO_2$/TFA (trifluoroacetic acid).[8] Further nitration of **5ga** under the same reaction conditions yielded the dinitro compound **5gg**. The synthesis of **5cg** was accomplished by reaction of the alcohol **3a(H)** with Cl_2SO[9] and nitration of the resulting chloride with NO_2BF_4.[10] The Friedel−Crafts reaction of the nitro compound **8** with *m*-fluoroanisole (**4c(F)**) yielded **5cg**. Compound **5dg** was obtained by solvolysis of **8** in *m*-fluorotoluene (**4d(F)**). Finally, the amines **5ab**, **5ba**, **5bb**, **5cb**, and **5db** were synthesized by catalytic hydrogenation of the nitro compounds **5ag**, **5ga**, **5gg**, **5cg**, and **5dg** using Pd/C as catalyst (Scheme 1).

UV Spectra and Semiempirical Calculations. Compound **6** shows a strong absorption at 228 nm (ϵ = 12 311) which is

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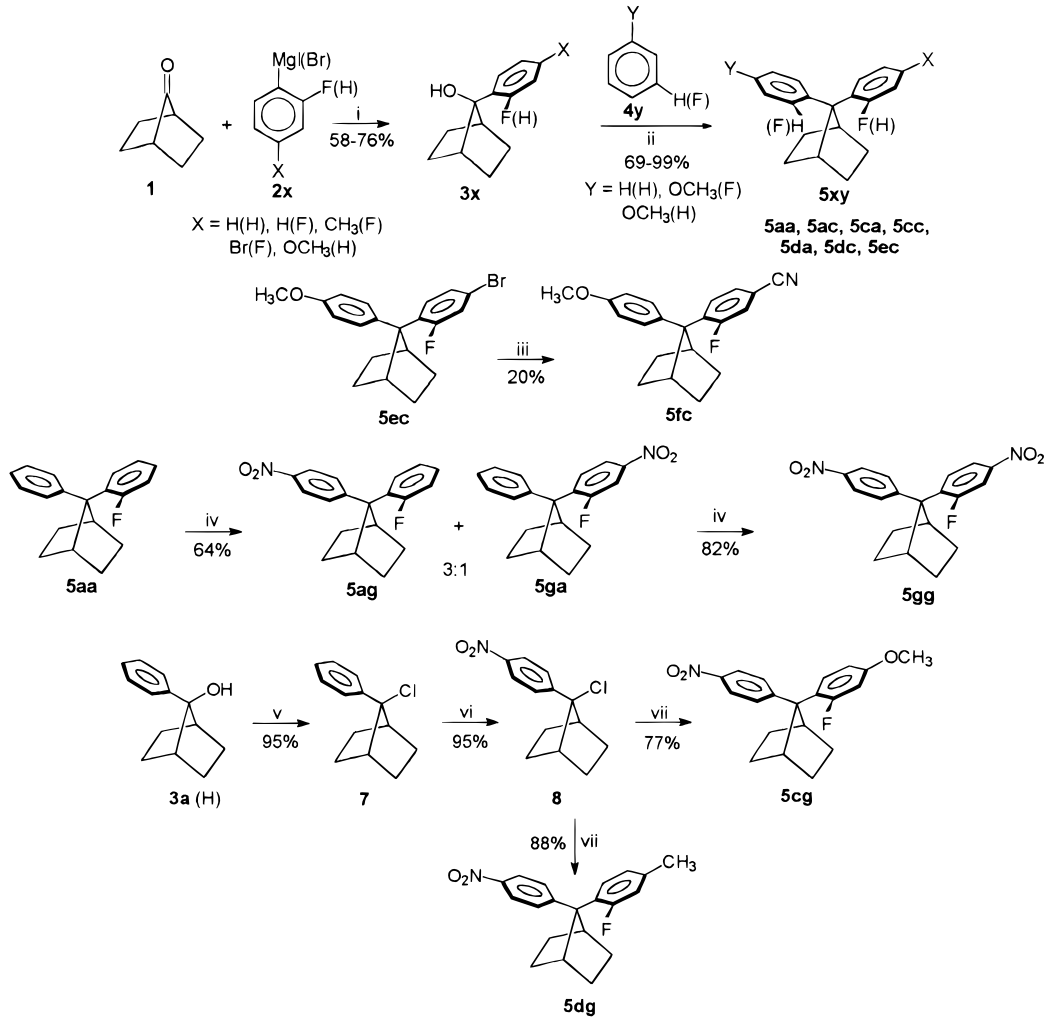
Scheme 1[a]



[a] Key: (i) (a) Et_2O or THF, Δ, Ar; (b) NH_4Cl; (ii) triflic acid, CH_2Cl_2, 25 °C, 1 h; (iii) (a) $(TPP)_2NiCl_2$, Zn, TPP, Δ, 1 h; (b) KCN, Δ, 10 h; (iv) $NaNO_2$, trifluoroacetic acid, 25 °C, 20 h; (v) Cl_2SO, Δ, 2 h; (vi) NO_2BF_4, 18-crown-6, CH_2Cl_2, 25 °C, Ar; (vii) $AlCl_3$, 25 °C, 2 h; (viii) H_2, Pd(C) (5%), Et_2O, 2 h.

not observed in the UV spectrum of 2,2-diphenylpropane (Figure 1), whose phenyl groups are arranged according to an helical (non-homoconjugated) conformation.[4]

The strong bands in the higher energy region of **6** have the characteristic aspect of aromatic conjugation bands (K bands). Moreover, according to calculations using the semiempirical AM1 method,[11] the electron density plot of **6** presents a bonding interaction between the C_{ipso} atoms of both rings (Figure 2a). Therefore, compound **6** is a π-homoconjugated structure and the absorption at 228 nm can be considered as the first example of an apical homoconjugation band (AHK band). The AHK band is the result of transitions between molecular orbitals (MOs) which are extended over both (planar) phenyl rings. These MOs are formed by mixing and splitting of aromatic MOs caused by strong electrostatic repulsions at short interannular distances.

The position of the AHK bands depends on the substituents, as shown in Table 1. The very electronegative F atom as well as the electron-withdrawing NO_2 group causes hypsochromic shifts. In compounds bearing these groups, the AHK band appears in the same region than the intraannular ^1L_a bands (p bands).[12] In the case of the electron donor groups CH_3, OCH_3, and NH_2, bathochromic shifts of the AHK band were observed, as expected for a conjugation band.[12] In the case of the donor−acceptor-substituted compounds **5cg** and **5fc**, a CT band appears as a strong and broad absorption in the lower energy region of the spectrum overlapping the intraannular ^1L_b band (α band). According to the AM1 method, there is a change in Ψ^2 values (charge density) of both rings of these compounds going from the HOMO to the LUMO, as showed in Figure 2 in the case of **5cg**. Weak absorptions at the lower energy region of the spectrum have been observed in other types of aromatic (lateral) homoconjugated compounds as well as stacked (including cyclophanes) arenes.[13] This bands are usually described as a transannular or charge transfer (CT) transitions.[13] Weak CT bands have been also observed in donor−acceptor-substituted diphenylmethanes, whose aryl groups are arranged in helical or orthogonal conformations.[14]

Molecular Mechanics Calculations. The potential energy (E_{st}) vs torsion angle $\varphi(C_{14}-C_7-C_8-C_9)$ function in the case of **5aa** was calculated using the MMX program[15] with energy minimization. The rotation takes place according to the one-ring-flip mechanism.[4] The two maxima correspond to the perpendicular conformations **5′aa** and **5″aa** (Figure 3). In these conformations, there are neither CT nor homoconjugative

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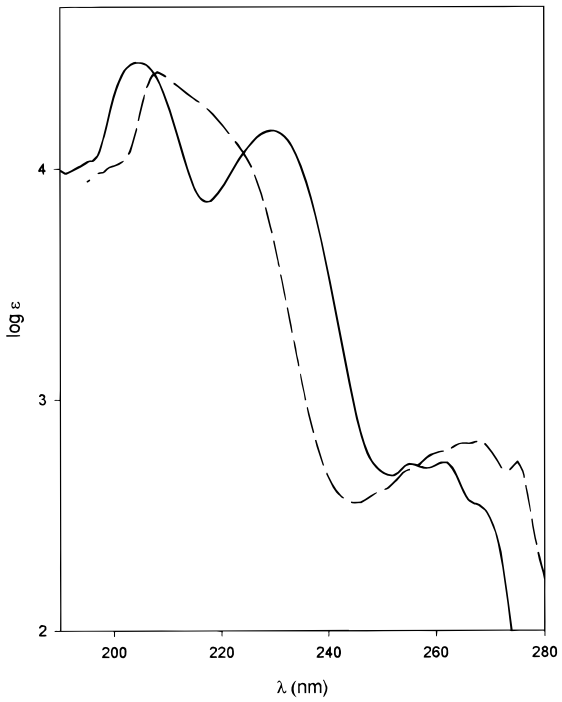

Figure 1. UV spectra (MeOH) of **6** and 2,2-diphenylpropane (dotted line).

interactions between both rings. The barrier for the rotation (17.0 kcal/mol) is higher than that calculated for 7,7-diphenylnorbornane (12.5 kcal/mol).[3]

Experimental Determination of Rotational Barriers by DNMR. The rotation barrier calculated by the MMX method (17.0 kcal/mol) for **5aa** is higher than the 160° libration barrier (14.4 kcal/mol) between **5aa** and *ent*-**5aa** over **5′aa** (see Figure 3). Thus, the 160° libration of the 2-fluorophenyl groups is the threshold movement exchanging the diasterotopic bridgehead protons H_1 and H_4. At room temperature, the libration is slow and the protons are anisochronous in the 300 MHz ^{1}H NMR spectra; a characteristic value for $\Delta\nu$ is about 100 Hz. The signals of H_1 and H_4 are slightly broadened by weak coupling with the vicinal protons. In all of the compounds **5xy**, the H_1 proton, which is *cis* positioned to the fluorine atom (see Figure 3), is downfield shifted in relation to the H_4 proton. The signals of the H_1 protons show a coupling of nearly 3 Hz with the fluorine nucleus. This is a new example of the recently described[16] H,F-dipolar coupling. In fact, the H_1-F distance (2.4 Å, MMX) is shorter than the sum of the van der Waals radii (2.5 Å).

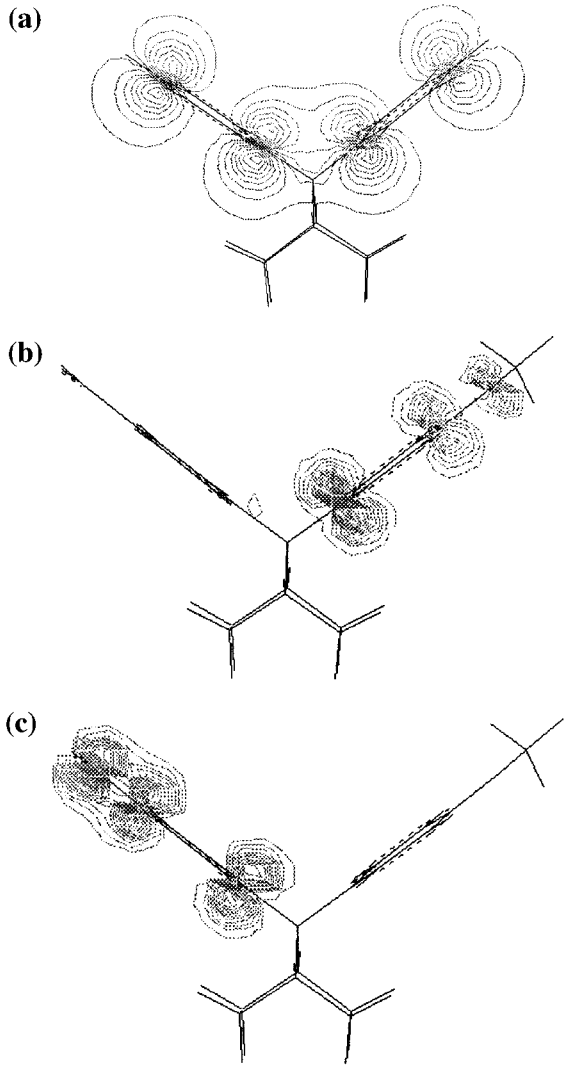

Figure 2. Electron density plot of **6** (a) and charge density of the HOMO (b) and LUMO (c) of **5cg**.

Warming of the sample in tetradeuterio-1,2-dichloroethane (CD_2Cl-CD_2Cl) resulted in the coalescence of the H_1 and H_4 signals. From the coalescence temperature (T_c range 337−356 K), the barrier for the 160° libration ($\Delta G^{\#}$) of the 2-fluoroaryl group of each compound was determined (Table 1). The accuracy of the $\Delta G^{\#}$ values was examined by line shape analysis. Due to negligible coupling of the H_4 (and H_1) signal, the function for the line shape is given by the Bloch equation for exchanging nucleus with no coupling.[17] The function $g(\nu)$ (line shape) was generated by the computer program DERIVE.[18] In order to check the reproducibility, some measurements were repeated at different days. The resulting experimental error was

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(18) DERIVE 2.59, Soft Warehouse, Honolulu, HI.

Table 1. Influence of the Substituents on the Libration Barriers and the Position of the AHK Band (in Methanol)

compound **5xy**	AHK (nm) (ϵ)	$\Delta G^{\#}$ (kcal/mol)[a]	$\Sigma\sigma_p$[b]	$\Delta G^{\#}_{cal}$ (kcal/mol)[c]	$\Delta G^{\#}_{cal} - \Delta G^{\#}$ (kcal/mol)
aa(H, H)	226 (12311)	17.0	0.00	17.00	0.0
ab(H, NH_2)	249 (10300)	17.2	−0.57	17.24	0.0
ac(H, OCH_3)	234 (15163)	17.1	−0.28	17.12	0.0
ag(H, NO_2)	221 (11042)[d]	16.6	0.81	16.66	0.1
ba(NH_2, H)	246 (10356)	16.5	−0.57	16.76	0.3
bb(NH_2,NH_2)	253 (12051)	16.6	−1.14	17.00	0.4
ca(OCH_3, H)	233 (14686)	16.6	−0.28	16.88	0.3
cb(OCH_3, NH_2)	247 (11986)	16.7	−0.85	17.12	0.4
cc(OCH_3, OCH_3)	238 (16909)	16.7	−0.56	17.00	0.3
cg(OCH_3, NO_2)[e]	223 (14531)	16.2	0.53	16.54	0.3
da(CH_3, H)	229 (13661)	16.8	−0.14	16.94	0.1
db(CH_3, NH_2)	247 (11448)	17.0	−0.71	17.18	0.2
dc(CH_3, OCH_3)	237 (14253)	16.9	−0.42	17.06	0.2
dg(CH_3, NO_2)	225 (8034)	16.4	0.67	16.60	0.2
ec(Br, OCH_3)	242 (16541)	17.0	−0.02	17.23	0.2
fc(CN, OCH_3)[f]	237 (12301)[d]	17.2	0.42	17.41	0.2
ga(NO_2, H)	222 (6350)[d]	17.1	0.81	17.34	0.2
gg(NO_2, NO_2)	224 (11438)[d]	16.8	1.62	17.00	0.2

[a] Experimental error ±0.1 kcal/mol. [b] Sum of σ_p of X and Y. [c] Calculated with eq 3. [d] Shoulder. [e] CT band between 290 and 330 nm (9240).[d] [f] CT band between 250 and 310 nm (7235).[d]

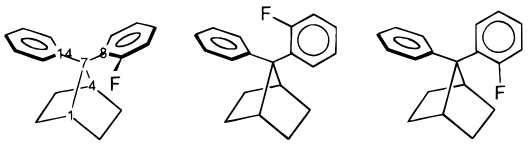

Figure 3. Relative energy vs torsion angle (φ) of the significant conformations of **5aa**.

±0.1 kcal/mol. According to statistical methods, barriers differing by 0.2 kcal/mol represent two distinct values with 95% probability.[19] On the other hand, the similar coalescence temperatures make unnecessary entropy corrections.[2]

Following the procedure of Cozzi *et al.*,[2] the experimental values were plotted vs the sum of σ_p for the substituents X and Y ($\Sigma\sigma_p$). The observed range of $\Delta G^{\#}$ (see Table 1) as well as the correlation coefficients *r* (see Figures 4−7) are similar to the described by Cozzi *et al.*[2] Surprisingly, two opposite linear correlation trends were observed. Thus, in the case of substituent X = constant and Y = variable, the slope is negative (Figures 4 and 5) (series 1). However, in the case of X = variable and Y = constant (series 2), the slope is positive (Figures 6 and 7), in agreement with the results of Cozzi *et al.*[2]

Discussion

The ΔE values calculated by the MMX method lie around 14.0 ± 0.5 kcal/mol, about 3 kcal/mol lower than the experimental barriers. Moreover, there is no correlation between ΔE and $\Delta G^{\#}$ values. At its actual sophistication level (and default values), the molecular mechanics methods cannot be satisfactorily used for the calculation of interactions between aromatic rings.

The positive slope observed in series 2 can be interpreted in terms of an electrostatic (Coulombic) interaction between the two aryl groups in the cofacial conformation of the type **5aa**.[2] Thus, substitution of hydrogen by an electron-donating group should increase the repulsion, raise the energy of this conformation, and, therefore, lower the $\Delta G^{\#}$ value. On the other hand,

(19) Young, H. D. *Statistical Treatment of Experimental Data*; McGraw-Hill: London, 1964.

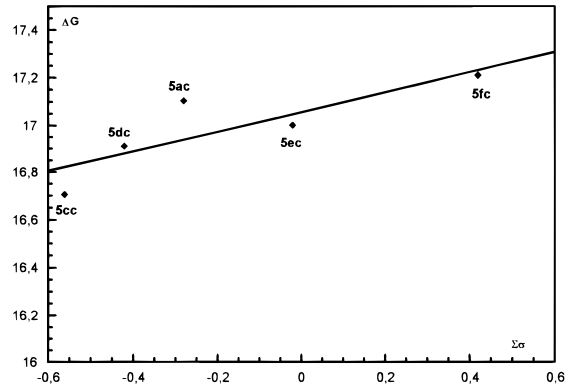

Figure 4. Plot of barrier to rotation ($\Delta G^{\#}$) vs $\Sigma\sigma_p$ for **5xy** (**y** = OCH_3; **x** = OCH_3 (**5cc**), CH_3 (**5dc**), H (**5ac**), Br (**5ec**), and CN (**5fc**) (series 1).

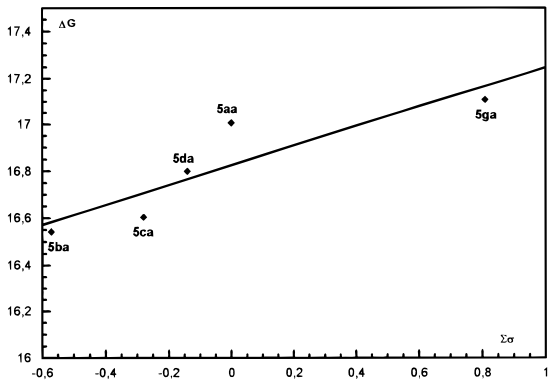

Figure 5. Plot of barrier to rotation ($\Delta G^{\#}$) vs $\Sigma\sigma_p$ for **5xy** (**y** = H; **x** = NH_2 (**5ba**), OCH_3 (**5ca**), CH_3 (**5da**), H (**5aa**), and NO_2 (**5ga**) (series 1).

electron-withdrawing groups should reduce the electrostatic repulsion of the cofacial conformation and raise the librational barrier. It is then obvious that the striking negative slope observed in series 1 cannot be accounted for by Coulombic interactions between the aryl groups only in the ground state conformation. On the other hand, neither charge-transfer nor homoconjugative interactions can explain the Hammet correlation between $\Delta G^{\#}$ and $\Sigma\sigma_p$ observed. In fact, both electron-donating and electron-withdrawing substituents should interact with the neutral phenyl ring (X or Y = H) and raise the libration

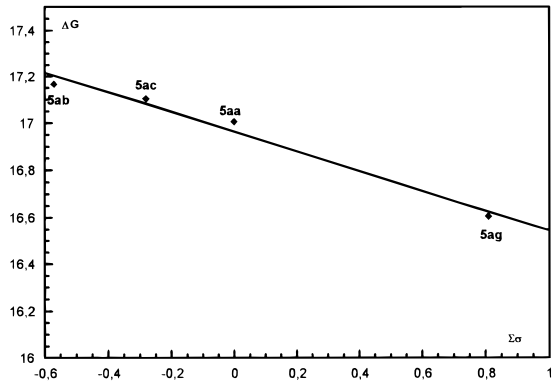

Figure 6. Plot of barrier to rotation ($\Delta G^{\#}$) vs $\Sigma\sigma_p$ for **5xy** (**x** = H; **y** = NH_2 (**5ab**), OCH_3 (**5ac**), H (**5aa**), and NO_2 (**5ag**) (series 2).

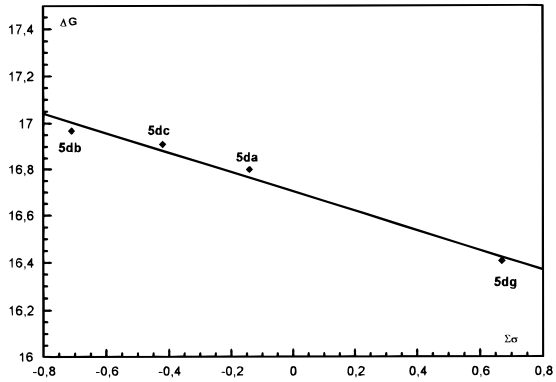

Figure 7. Plot of barrier to rotation ($\Delta G^{\#}$) vs $\Sigma\sigma_p$ for **5xy** (**x** = CH_3; **y** = NH_2 (**5db**), OCH_3 (**5dc**), H (**5da**), and NO_2 (**5dg**) (series 2).

barrier.[2] Particularly high $\Delta G^{\#}$ values should be obtained in the cases of the donor−acceptor-substituted substrates **5cg** and **5fc** (Table 1), an assumption that does not agree with our results.

In our opinion, the negative slope in series 1 shows that the electrostatic interaction in the transition state (conformation of the type **5′aa**) cannot be omitted. In fact, the repulsive interaction between fluorine and the opposite aryl ring (n,π-repulsion)[20] should be independent of the substituent X, but dependent on the electronic properties of the substituent Y. Thus, the general Hammett function for the correlation between $\Delta G^{\#}$ and σ_p of the aryl substituents should be (eq 1)

$$\Delta G^{\#} = m(\sigma_p^{x} + \sigma_p^{y}) - n(\sigma_p^{y}) + \Delta G^{\#}_{o} \qquad (1)$$

If $\sigma_p^{x} = \sigma_p^{y} = 0$, then $\Delta G^{\#} = \Delta G^{\#}_{o}$ which corresponds to the measured barrier in the case of the parent compound **5aa** (17.0 kcal/mol). On the other hand, a value of 0.42 for *m* can be determined from the slopes obtained when $\sigma_p^{y} = 0$ and σ_p^{x} = variable (Figure 6). It then follows that

$$\Delta G^{\#} = 0.42\sigma_p^{x} + (0.42-n)\sigma_p^{y} + 17.0 \qquad (2)$$

From the slope (−0.42) in the case $\sigma_p^{x} = 0$ and σ_p^{y} = variable (Figure 5), a value of $n = 0.84$ is obtained and therefore

$$\Delta G^{\#} = 0.42(\sigma_p^{x} - \sigma_p^{y}) + 17.0 \qquad (3)$$

The barriers ($\Delta G^{\#}_{cal}$) calculated with the eq 3 are given in Table 1. The standard deviation (0.2) of the differences $\Delta G^{\#}_{cal} - \Delta G^{\#}$ corresponds to the expected value, taking into account the experimental error in the measurement of $\Delta G^{\#}$ (±0.1 kcal/mol). Significative deviations ($\Delta G^{\#}_{cal} - \Delta G^{\#} = 2 \times 0.2$ kcal/mol) were found in two cases, **5bb** and **5cb**. Systematic deviations were found only for those substrates bearing two strong donating substituents, pointing to a higher electrostatic interaction in the ground state than that measured by $\Sigma\sigma_p$.

In our substrates **5xy**, the Coulombic interactions in the transition state are stronger than in the 1,8-diarylnaphthalene derivatives studied by Cozzi *et al.*,[2] due to the π,*n*-repulsion caused by the fluorine atom at the rotating ring. However, Coulombic interactions in the transition state are also operative in Cozzi's substrates. Thus, the lower slope observed in the case of *p*,*p*′-disubstituted substrates ($\Delta G^{\#}$ range of 24.0−25.4 kcal/mol)[2b] in relation to the higher slope in the case of *p*-substituted substrates ($\Delta G^{\#}$ range of 13.9−17.3 kcal/mol)[2c] can be accounted for by the canceling effect of the substituent at the nonrotating ring on $\Delta G^{\#}$ (eq 1) in the case of the disubstituted substrates.

Summary and Conclusions

There is spectroscopic evidence (UV absorption) of homoconjugative interaction between the aryl rings in the 7,7-diarylnorbornane system. This interaction is also detected by semiempirical calculations showing a bonding interaction between the C_{ipso} atoms of both rings. The proximity of the aryl rings favors CT transitions also, which are revealed by the corresponding absorption bands in the UV spectra of donor−acceptor-substituted compounds **5xy**. According to the AM1 method, such transitions take place in the lower energy region of the spectrum (CT bands).

However, the existing Hammett correlation between the librational barriers of **5xy** precludes any significant stabilization of the cofacial conformation of **5xy** neither by homoconjugation nor by CT interactions. Thus, the librational barriers can be accounted for only in terms of transannular Coulombic interactions. The following can be concluded.

First, even at the short interannular distance of 2.8 Å, the homoconjugative attractive interaction is always overcome by the Coulombic repulsion. It is not possible that homoconjugative interactions could be widely independent of the nature of the substituents, because the frequency of the AHK bands depend on it. Second, like other interactions between filled MOs,[21] the homoconjugated aromatic π,π-interaction provokes considerable changes in the electronic spectrum, but little (or no) global stabilization. Third, there is no appreciable contribution of CT configurations to the ground state of **5xy**. Fourth, Coulombic interactions are also operative in the transition state of the one-ring-flip mechanism for the rotation in diarylmethanes. Therefore, the notion of homoconjugation as well as CT as short-range stabilizing interactions should be rejected.[2,22,23]

Experimental Section

General Procedures. Melting points (mp = °C) were measured in a Gallenkamp melting point apparatus and are uncorrected. All reactions involving organometallic reagents were carried out under an argon atmosphere. Solvents were dried by distillation over the following drying agents: diethyl ether and THF (Na/benzophenone),

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DMF (calcium hydride), methylene chloride (phosphorous pentoxide). Starting materials and reagents obtained from commercial sources were used without further purification. Flash chromatography was performed over Merck silica gel 60 (230−400 mesh).

NMR spectra were recorded on a Varian XL 300 (299.94 MHz for ^{1}H and 75.43 MHz for ^{13}C) spectrometer and a Brucker-AC 250 (250.13 MHz for ^{1}H and 62.90 MHz for ^{13}C) spectrometer. The rotational barriers of compounds **5xy** were determined by variable-temperature experiments in the Varian XL 300 spectrometer in tetradeuterio-1,2-dichloroethane. Chemical shifts (δ) are given in ppm relative to TMS and coupling constants (J) are given in Hz. IR spectra were recorded in a Perkin-Elmer 781 spectrometer. Wavenumbers are in cm^{-1}. Mass spectra were recorded on a GC-MS HP-5989 (60 eV) mass spectrometer. For gas chromatography, a Perkin-Elmer 300 chromatograph equipped with capillary OV 101 column was used. UV spectra were measured in a Perkin-Elmer Lambda-3 spectrometer using methanol as solvent. Wavelengths are in nm.

Substrates. 7- Norbornanone (**1**)[24] and $(TPP)_2NiCl_2$[25] were prepared according to the procedures described in the literature.

General Procedure for the Synthesis of Alcohols 3x. A solution of 3.03 g (13.7 mmol) of 1-fluoro-2-iodobenzene in 20 mL of anhydrous diethyl ether and a solution of 1 g (9.09 mmol) of 7-norbornanone (**1**) in 20 mL of anhydrous diethyl ether were added simultaneously over a suspension of 0.33 g (13.7 mmol) of magnesium turnings in 50 mL of anhydrous diethyl ether.[26] After 3 h of reflux, 50 mL of saturated ammonium chloride solution was added. The reaction mixture was extracted with ether (3 × 25 mL) and dried over magnesium sulfate. After concentration at reduced pressure, the alcohols **3x** were purified by flash chromatography (hexane/diethyl ether 15:1). For the reaction with 4-bromo-3-fluoroanisole, the reaction was carried out using THF as solvent.

7-Phenyl-7-norbornanol (3a(H)):[27] (76%); oil; ^{1}H NMR δ 7.50 (d, 2H, J = 6.9), 7.37 (t, 2H, J = 6.9), 7.30 (t, 1H, J = 6.9), 2.4 (m, 2H), 2.18 (m, 2H), 1.70 (s, 1H), 1.43 (m, 4H), 1.22 (m, 2H).

7-(2-Fluorophenyl)-7-norbornanol (3a(F)): (58%); mp = 65.4−67.2; ^{1}H NMR δ 7.57−7.00 (m, 4H), 2.63−2.52 (m, 2H), 2.20−2.08 (m, 2H), 2.05 (s, 1H), 1.55−1.18 (m, 6H).

7-(2-Fluoro-4-methylphenyl)-7-norbornanol (3d(F)): (60%); mp = 63.1−65.9; ^{1}H NMR δ 7.31 (t, 1H, J =8.0), 6.95−6.83 (m, 2H), 2.58−2.50 (m, 2H), 2.33 (s, 3H), 2.19−2.05 (m, 2H), 1.97 (s, 1H), 1.53−1.20 (m, 6H).

7-(4-Bromo-2-fluorophenyl)-7-norbornanol (3e(F)): (62%); mp = 75.8−78.1; ^{1}H NMR δ 7.33 (t, 1H, J = 8.1), 7.28−7.22 (m, 2H), 2.55−2.45 (m, 2H), 2.16−2.06 (m, 2H), 2.00 (s, 1H), 1.48−1.20 (m, 6H).

7-(4-Methoxyphenyl)-7-norbornanol (3c(H)): (74%); mp = 56.1−58.3; ^{1}H NMR δ 7.40 (d, 2H, J = 8.8), 6.90 (d, 2H, J = 8.8), 3.80 (s, 3H), 2.40−2.30 (m, 2H), 2.20−2.10 (m, 2H), 1.58 (s, 1H), 1.50−1.15 (m, 6H).

Synthesis of Compounds 5xy from Alcohols 3x. To a solution of 1 mmol of the corresponding alcohol **3x** in 10 mL of benzene (**5aa** and **5da**), anisole (**5ac**, **5dc** and **5ec**) or *m*-fluoroanisole (**5ca** and **5cc**) were added 0.15 g (1 mmol) of trifluoromethanosulfonic (triflic) acid. After 2 h of stirring at room temperature, 50 mL of methylene chloride was added and the reaction mixture was washed with water (2 × 40 mL) and dried over magnesium sulfate. The solvent was evaporated at reduced pressure, and the residue was purified by flash chromatography: **5aa** and **5da**, hexane; **5ac**, **5dc**, **5ec**, and **5ca**, hexane/methylene chloride 10:1; **5cc**, hexane/methylene chloride 10:4.

7-(2-Fluorophenyl)-7-phenylnorbornane (5aa): (76%); mp = 145.1−148.0 (methanol); ^{1}H NMR δ 7.52−7.44 (m, 3H), 7.22 (t, 2H, J = 7.8), 7.12−6.97 (m, 3H), 6.86 (ddd, 1H, J = 11.9, 8.4, 2.0), 3.41 (q, 1H, J = 3.3), 3.07 (t, 1H, J = 3.3), 1.83−1.20 (m, 8H).

7-(2-Fluoro-4-methylphenyl)-7-phenylnorbornane (5da): (99%); mp = 129.0−130.2; ^{1}H NMR δ 7.45 (d, 2H, J = 7.5), 7.33 (t, 1H, J = 8.4), 7.20 (t, 2H, J = 7.5), 7.07 (t, 1H, J = 7.5), 6.81 (dd, 1H, J = 8.4, 2.7), 6.68 (ddd, 1H, J = 12.6, 2.7, 0.6), 3.40 (q, 1H, J = 4.3), 3.08 (t, 1H, J = 3.7), 2.22 (s, 3H), 1.85−1.20 (m, 8H).

7-(2-Fluorophenyl)-7-(4-methoxyphenyl)norbornane (5ac): (80%); mp = 74.1−75.5; ^{1}H NMR δ 7.39 (dd, 2H, J = 8.8, 1.2), 7.30 (td, 1H, J = 9.0, 1.3), 6.83−6.68 (m, 5H), 3.53 (q, 1H, J = 4.1), 3.27 (s, 3H), 2.85 (t, 1H, J = 3.9), 1.92−1.50 (m, 4H), 1.38−1.08 (m, 4H).

7-(2-Fluoro-4-methylphenyl)-7-(4-methoxyphenyl)norbornane (5dc): (94%); mp = 108.0−109.0; ^{1}H NMR δ 7.36 (dd, 2H, J = 9.0, 1.5), 7.32 (t, 1H, J = 8.1), 6.82−6.81 (ddd, 1H, J = 8.1, 1.5, 0.6), 6.74 (d, 2H, J = 9.0), 6.71−6.65 (dd, 1H, J = 12.6, 1.5), 3.71 (s, 3H), 3.33 (q, 1H, J = 4.3), 3.00 (t, 1H, J = 3.9), 2.21 (s, 3H), 1.80−1.16 (m, 8H).

7-(4-Bromo-2- fluorophenyl)-7-(4-methoxyphenyl)norbornane (5ec): (83%); mp = 133.4−134.8; ^{1}H NMR δ 7.40−7.30 (m, 3H), 7.15 (dd, 1H, J = 8.6, 2.1), 7.08 (ddd, 1H, J = 11.1, 2.1, 0.6), 6.75 (d, 2H, J = 8.9), 3.75 (s, 3H), 3.30 (q, 1H, J = 4.2), 3.00 (t, 1H, J = 3.7), 1.80−1.20 (m, 8H).

7-(2-Fluoro-4-methoxyphenyl)-7-phenylnorbornane (5ca): (90%); mp = 94.4−96.0; ^{1}H NMR δ 7.44 (d, 2H, J = 8.1), 7.35 (t, 1H, J = 9.0), 7.21 (t, 2H, J = 8.1), 7.08 (t, 1H, J = 8.1), 6.58 (dd, 1H, J = 9.0, 2.7), 6.44 (ddd, 1H, J = 13.5, 2.7, 0.6), 3.69 (s, 1H), 3.36 (q, 1H, J = 4.3), 3.02 (t, 1H, J = 3.7), 1.80 −1.20 (m, 8H).

7-(2-Fluoro-4-methoxyphenyl)-7-(4-methoxyphenyl)norbornane (5cc): (69%); mp = 141.1−142.2; ^{1}H NMR δ 7.35 (dd, 2H, J = 8.8, 1.5), 7.30 (t, 1H, J = 16.0), 6.75 (d, 2H, J = 8.8), 6.57 (dd, 1H, J = 8.5, 2.4), 6.44 (dd, 1H, J = 13.4, 2.7), 3.72 (s, 3H), 3.69 (s, 3H), 3.31 (q, 1H, J = 4.3), 2.98 (t, 1H, J = 3.9), 1.80−1.15 (m, 8H).

7-(4-Cyano-2-fluorophenyl)-7-(4-methoxyphenyl)norbornane (5fc). A mixture of 0.083 g (1.37 mmol) of $(TPP)_2NiCl_2$,[25] 0.010 g (1.37 mmol) of zinc powder, and 0.066 g (2.74 mmol) of triphenylphosphine (TPP) was refluxed for 1 h under an argon atmosphere.[7] During this time, the color of the reaction mixture changed from blue to red; 0.5 g (1.37 mmol) of **5ec** and 0.083 g (1.37 mmol) of potassium cyanide (in small portions) were then added to the reaction mixture. After 3 h the reaction was diluted with 20 mL of methylene chloride and poured over 30 mL of water. The organic layer was separated and dried over magnesium sulfate. After evaporation of the solvent under reduced pressure and purification of the residue by flash chromatography (hexane/methylene chloride 10 :1), 0.09 g (20%) of **5fc** was obtained: mp = 131.4−133.6; ^{1}H NMR δ 7.60 (t, 1H, J = 7.9), 7.40−7.30 (m, 3H), 7.20 (dd, 1H, J = 11.0, 1.7), 6.80 (d, 2H, J = 8.9), 3.75 (s, 3H), 3.40 (q, 1H, J = 4.3), 3.10 (t, 1H, J = 3.8), 1.80−1.20 (m, 8H).

7-(2-Fluorophenyl)-7-(4-nitrophenyl)norbornane (5ag) and 7-(2-Fluoro-4-nitrophenyl)-7-phenylnorbornane (5 ga). To a suspension of 0.27 g (1 mmol) of **5aa** in 10 mL of trifluoroacetic acid (TFA) was added 0.07 g (1 mmol) of $NaNO_2$.[8] After 20 h of stirring at room temperature, the reaction mixture was diluted with 50 mL of methylene chloride, washed with water (2 × 20 mL), and dried over magnesium sulfate. After evaporation of the solvent at reduced pressure and separation of the products by flash chromatography (hexane/methylene chloride 15:1), 0.15 g (48%) of **5ag** and 0.05 g (16%) of **5ga** were obtained.

7-(2-Fluorophenyl)-7-(4-nitrophenyl)norbornane (5ag): mp = 159.0−159.7; ^{1}H NMR δ 8.09 (d, 2H, J = 9.0), 7.63 (dd, 2H, J = 9.0, 1.2), 7.48 (td, 1H, J = 7.5, 2.1), 7.18−7.02 (m, 2H), 6.90 (ddd, 1H, J = 12.0, 8.1, 1.5), 3.42 (q, 1H, J = 4.2), 3.10 (t, 1H, J = 3.6), 1.90−1.20 (m, 8H).

7-(2-Fluoro-4-nitrophenyl)-7-phenylnorbornane (5ga): mp = 98.3−100.1; ^{1}H NMR δ 7.93 (ddd, 1H, J = 9.0, 2.4, 0.6), 7.77 (dd, 1H, J = 11.1, 2.4), 7.68 (dd, 1H, J = 9.0, 7.8), 7.45 (d, 2H, J = 8.4), 7.25 (t, 2H, J = 8.4), 7.14 (t, 1H, J = 8.4), 3.43 (q, 1H, J = 4.3), 3.10 (t, 1H, J = 3.7), 1.83−1.20 (m, 8H).

7-(2-Fluoro-4-nitrophenyl)-7-(4-nitrophenyl)norbornane (5gg): Following the procedure described previously, 0.31 g (1mmol) of **5ga**

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were nitrated using 0.07 g (1 mmol) of $NaNO_2$. After purification by flash chromatography, (hexane/methylene chloride 15 :1), 0.28 g (82%) of **5gg** was obtained; mp = 187.8−188.9; ^{1}H NMR δ 8.13 (d, 2H, J = 9.0), 7.97 (ddd, 1H, J = 8.7, 2.4, 0.6), 7.80 (dd, 1H, J = 11,1, 2.4), 7.70 (t, 1H, J = 8.7), 7.63 (dd, 2H, J = 9.0, 1.2), 3.47 (q, 1H, J = 4.1), 3.18 (t, 1H, J = 3.7), 1.80−1.20 (m, 8H).

7-Chloro-7-phenylnorbornane (7).[27] A mixture of 0.27 g (1.33 mmol) of **3a(H)** and 0.47 g (3.99 mmol) of thionyl chloride was refluxed for 1 h.[9] After addition of 10 mL of benzene and evaporation of the solvent and excess thionyl chloride at reduced pressure, the residue was purified by flash chromatography (hexane) or sublimation; 0.31 g (95%) of **7** were obtained; mp = 91.5−93.2; ^{1}H NMR δ 7.48 (d, 2H, J = 6.9), 7.35 (t, 2H, J = 6.9), 7.27 (t, 1H, J = 6.9), 2.79 (m, 2H), 2.35−2.20 (m, 2H), 1.60−1.40 (m, 4H), 1.40−1.20 (m, 2H).

7-Chloro-7-(4-nitrophenyl)norbornane (8). To a solution of 0.27 g (1.33 mmol) of **7** and 0.010 g (0.04 mmol) of 18-crown-6 in 15 mL of methylene chloride was added 0.18 g (1.33 mmol) of NO_2BF_4 under an argon atmosphere.[10] After 1 h of stirring, 50 mL of methylene chloride was added and the resulting solution was washed with water (2 × 20 mL) and dried over magnesium sulfate. The solvent was evaporated at reduced pressure, and the residue was purified by flash chromatography (hexane/methylene chloride 10:1), affording 0.29 g (95%) of **8**: mp = 176.7−178.2; ^{1}H NMR δ 8.25 (d, 2H, J = 8.5), 7.65 (d, 2H, J = 8.5), 2.80−2.70 (m, 2H), 2.35−2.20 (m, 2H), 1.60−1.40 (m, 6H).

7-(2-Fluoro-4-methoxyphenyl)-7-(4-nitrophenyl)norbornane (5cg). To a solution of 0.25 g (1 mmol) of **8** in 10 mL of *m*-fluoroanisole was added 0.15 g (1.1 mmol) of aluminium trichloride. After 2 h of stirring at room temperature, the reaction mixture was diluted with 50 mL of methylene chloride, washed with water (2 × 40 mL), and dried over magnesium sulfate. The solvent was evaporated at reduced pressure, and after purification by flash chromatography (hexane/methylene chloride 10 :1), 0.26 g (77%) of **5cg** was obtained: mp = 158.6−160.2; ^{1}H NMR δ 8.10 (d, 2H, J = 9.0), 7.60 (dd, 2H, J = 9.0, 1.2), 7.34 (t, 1H, J = 8,7), 6.61 (dd, 1H, J = 8.7, 2.7), 6.46 (dd, 1H, J = 13.5, 2.7), 3.72 (s, 3H), 3.37 (q, 1H, J = 4.2), 3.05 (t, 1H, J = 3.6), 1.90−1.20 (m, 8H).

7-(2-Fluoro-4-methylphenyl)-7-(4-nitrophenyl)norbornane (5dg). Following the procedure described for the synthesis of **5cg**, using *m*-fluorotoluene as solvent, **5dg** was prepared in 88% yield: mp = 161.0−163.0; ^{1}H NMR δ 8.08 (d, 2H, J = 9.0), 7.61 (dd, 2H, J = 9.0, 1.2), 7.33 (t, 1H, J = 8.3), 6.86 (ddd, 1H, J = 8.3, 1.7, 0.7), 6.72 (dd, 1H, J = 12.9, 1.0), 3.40 (q, 1H, J = 4.1), 3.08 (t, 1H, J = 3.7), 2.10 (s, 3H), 1.85−1.20 (m, 8H).

General Procedure for the Synthesis of the Amines 5ab, 5ba, 5bb, 5cb, and 5db. A solution of 1 mmol of the corresponding nitro compound **5ag**, **5ga**, **5gg**, **5cg**, or **5dg** in 200 mL of diethyl ether was hydrogenated at 1 atm of pressure using 60 mg of 5% Pd/C. The catalyst was filtered off, and the solvent was evaporated at reduced pressure. The amines were obtained quantitatively.

7-(2-Fluorophenyl)-7-(4-aminophenyl)norbornane (5ab): mp = 130.0−132.0; ^{1}H NMR δ 7.44 (td, 1H, J = 7.8, 1.8), 7.24 (dd, 2H, J = 7.2, 1.5), 7.08−6.98 (m, 1H), 6.85 (ddd, 1H, J = 12.0, 7.8, 1.5), 6.55 (d, 2H, J = 7.2), 3.40 (s, 1H), 3.30 (q, 1H, J = 4.8), 3.00 (t, 1H, J = 3.9), 1.80−1.20 (m, 8H).

7-(4-Amino-2-fluorophenyl)-7-phenylnorbornane (5ba): mp = 120.8−123.4; ^{1}H NMR δ 7.44 (d, 2H, J = 8.4), 7.30−7.10 (m, 3H), 7.08 (t, 1H, J = 8.4), 6.32 (dd, 1H, J = 8.1, 2.4), 6.20 (dd, 1H, J = 13.2, 2.4), 3.70−3.30 (m, 3H), 3.00 (t, 1H, J = 3.7), 1.80−1.20 (m, 8H).

7-(4-Amino-2-fluorophenyl)-7-(4-aminophenyl)norbornane (5bb): mp = 150.0−152.0; ^{1}H NMR δ 7.19 (dd, 2H, J = 8.7, 1.2), 7.16 (t, 1H, J = 8.1), 6.55 (d, 2H, J = 8.7), 6.32 (dd, 1H, J = 8.1, 2.4), 6.20 (dd, 1H, J = 13.2, 2.4), 3.35 (s, 4H), 3.25 (q, 1H, J = 4.2), 2.94 (t, 1H, J = 3.7), 1.80−1.20 (m, 8H).

7-(2-Fluoro-4-methoxyphenyl)-7-(4-aminophenyl)norbornane (5cb): mp = 133.4−136.1; ^{1}H NMR δ 7.30 (t, 1H, J = 9.0), 7.20 (dd, 2H, J = 6.9, 1.5), 6.60−6.50 (m, 3H), 6.43 (dd, 1H, J = 13.2, 2.7), 3.68 (s, 3H), 3.30−3.20 (m, 3H), 2.9 (t, 1H, J = 3.8), 1.85−1.14 (m, 8H).

7-(2-Fluoro-4-methylphenyl)-7-(4-aminophenyl)norbornane (5db): mp = 147.1−149.2; ^{1}H NMR δ 7.30 (t, 1H, J = 8.2), 7.22 (dd, 2H, J = 7.7, 1.2), 6.80 (dd, 1H, J = 8.2, 1.0), 6.70 (dd, 1H, J = 12.9, 1.0), 6.54 (d, 2H, J = 7.7), 3.40 (s, 2H), 3.30 (q, 1H, J = 4.2), 2.97 (t, 1H, 3.2), 2.20 (s, 3H), 1.80−1.20 (m, 8H).

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Supporting Information Available: Spectroscopic data (IR, ^{13}C NMR, MS) of compounds **3x**, **5xy**, **7**, and **8** (7 pages). See any current masthead page for ordering and Internet access instructions.

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