over $MgSO_4$ and removal of solvent gave a white solid. Preparative layer chromatography (PLC) (50% ethyl acetate:hexane, silica gel) gave 346 mg (99%) of a white solid: mp 93–94 °C; ^1H NMR ($CDCl_3$) δ 7.95–8.25 (m, 2 H), 7.35–7.60 (m, 2 H), 6.70–7.25 (m, 5 H), 4.03 (s, 2 H); IR (Nujol) 1055 cm^{-1} (S=O).

Anal. Calcd for $C_{13}H_{11}O_3NS$: C, 59.76; H, 4.24; N, 5.36; S, 12.27. Found: C, 59.56; H, 4.20; N, 5.16; S, 12.40.

A similar procedure afforded sulfoxide **10** in a 95% yield, isolated by PLC as a colorless oil: ^1H NMR ($CDCl_3$) δ 7.40 (d, 2 H, J = 9 Hz), 6.85 (d, 2 H, J = 9 Hz), 3.73 (s, 3 H), 2.73 (t, 2 H, J = 7 Hz), 1.20–1.80 (m, 4 H), 0.70–1.10 (m, 3 H); IR (neat) 1045 cm^{-1} (S=O).

Anal. Calcd for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.60; S, 15.10. Found: C, 61.92; H, 7.50; S, 14.94.

Sulfoxide **9** was formed in a similar fashion in 93% yield, mp 108–110 °C (lit.[15] mp 107–107.5 °C).

Typical Procedure for Sulfoxide Reduction. Di-*p*-tolyl sulfoxide (**5**) (288 mg, 1.25 mmol) was added to a 50-mL three-necked flask that had been thoroughly flushed with N_2; 15 mL of THF were then added, followed by 0.61 g of polystyryldiphenylphosphine (2.00 mmol contained P). CCl_4, 0.48 mL (5.00 mmol), was added and a reflux was started immediately. TLC (50% ether:hexane, silica gel) after 1.5 h revealed complete consumption of sulfoxide and formation of a single product of high R_f. The polymer was removed by filtration and washed thoroughly with 40 mL of ether. After brief drying over $MgSO_4$, the solvent was removed under reduced pressure. PLC (50% ether:hexane) yielded 266 mg (99%) of a white solid, mp 54–56 °C (lit.[16] mp 57.3 °C).

With the exception of sulfoxide **10**, all substrates afforded the desired sulfides by utilizing this procedure and the reaction times indicated in Table I. The spectral characteristics of all products matched those of the known compounds.

Sulfoxide **10** was much slower in reaction with an estimated 50% completion after a 5-h reflux by using the same ratio of reactants as above. Addition of additional amounts of reagents to bring the molar ratio to 1:3.2:8.0 (sulfoxide:phosphine:CCl_4) resulted in complete reaction after an additional 1-h reflux. PLC (20% ether:hexane) afforded an 85% yield of a colorless oil: ^1H NMR ($CDCl_3$) δ 7.17 (d, 2 H, J = 9 Hz), 6.67 (d, 2 H, J = 9 Hz), 3.68 (s, 3 H), 2.77 (t, 2 H, J = 7 Hz), 1.10–1.70 (m, 4 H), 0.70–1.00 (m, 3 H).

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33. Found: C, 67.30; H, 8.15; S, 16.42.

Acknowledgment. This work was generously supported by Research Corp. (Grant C1187).

Registry No. 1, 67-68-5; 2, 2168-93-6; 3, 945-51-7; 4, 3085-42-5; 5, 1774-35-2; 6, 621-08-9; 7, 20451-53-0; 8, 95217-44-0; 9, 955-45-3; 10, 78597-97-4; 1 (sulfide), 75-18-3; 2 (sulfide), 544-40-1; 3 (sulfide), 139-66-2; 4 (sulfide), 5181-10-2; 5 (sulfide), 620-94-0; 6 (sulfide), 538-74-9; 7 (sulfide), 1822-73-7; 8 (sulfide), 87740-10-1; 9 (sulfide), 952-97-6; 10 (sulfide), 78597-95-2; poly(styryldiphenylphosphine), 95217-45-1; CCl_4, 56-23-5.

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Attractive Nonbonded Interactions. The Solution Conformation of 1,2-Bis(pentafluorophenyl)-1,2-bis(*p*-methoxyphenyl)ethane

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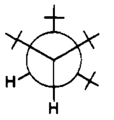
The tetrasubstituted ethanes **1** and **2** adopt, exclusively, an ethane H–H gauche conformation,[1] whereas 2,3-dimethylbutane exists in a statistical (2:1) ratio of the ethane H–H gauche and anti conformations.[2] Thus, 1,1,2,2-tetraalkylethanes prefer the gauche conformation with the preference increasing as the bulk of the alkyl groups increases. In contrast to the tetraalkylethanes, tetraarylethanes, e.g., 1,1,2,2-tetraphenylethane, prefer the ethane H–H anti conformation.[3] Empirical force field calculations predict for tetraphenylethane that the lowest energy gauche conformation is ~5 kcal/mol less stable than the anti form.[4]



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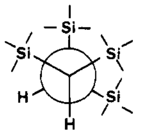

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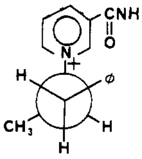

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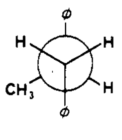

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We have recently discovered[5] a case in which polar interactions reverse a conformational preference; *N*-(1-phenyl-2-propyl)nicotinamide chloride (**3**) prefers the aryl–aryl gauche, aryl–methyl anti conformation, whereas its carbon analogue 1,2-diphenylpropane (**4**) prefers the aryl–aryl anti conformation.[6] In the former case the free energy difference between the more stable gauche conformer and the anti conformer is –0.66 kcal/mol while in the latter case the difference is 0.24 kcal/mol.[7] If the energy differences between conformations in similarly substituted systems is sufficiently small, as in the cases above, polar contributions may be sufficient to alter expected conformations. In the tetraarylethane series, polar effects have been probed in a study of the diastereomeric 1,2-diphenyl-1,2-di-4-pyridylethanes, both of which were demonstrated to exist predominantly in the H–H anti form.[8]

Numerous aryl–aryl complexes of hexafluorobenzene with donor aromatic molecules have been reported, e.g., hexafluorobenzene with benzene,[9] mesitylene,[10] hexamethylbenzene,[11,12] *p*-xylene,[13] and durene,[14] to mention but a few. Perhaps the most unexpected behavior is exhibited by an equimolar mixture of hexafluorobenzene and benzene; both pure compounds melt at ca. 5 °C and both boil at ca. 80 °C, yet the equimolar mixture melts at 23.7 °C.[9] Postulating that in appropriately substituted tetraarylethanes attractive ring–ring interactions of the perfluorobenzene–benzene type might suffice to alter the expected H–H anti predominance observed in other tetraarylethanes, the diastereomeric (*meso* and *dl*) 1,2-bis(*p*-methoxyphenyl)-1,2-bis(pentafluorophenyl)ethanes

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[7] These estimates are based on calculated conformer populations and are subject to error depending upon the selection of "theoretical" coupling constants employed in the calculation.

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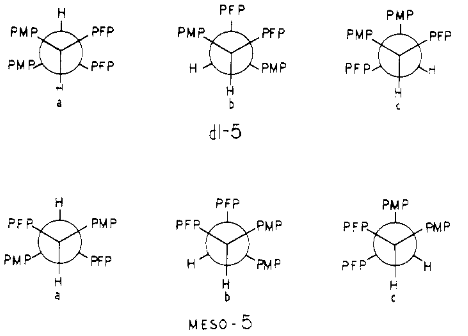

Figure 1. Conformations of 1,2-bis(pentafluorophenyl)-1,2-bis(*p*-methoxyphenyl)ethane. PMP = *p*-methoxyphenyl; PFP = perfluorophenyl.

were prepared and analyzed.

(Pentafluorophenyl)(*p*-methoxyphenyl)methanol was coupled in the presence of chromium(II) chloride to yield an equimolar (by NMR analysis) mixture of the diastereomeric 1,2-bis(*p*-methoxyphenyl)-1,2-bis(pentafluorophenyl)ethanes (*meso*- and *dl*-**5**).[15] The separation of the diastereomers was readily accomplished by successive crystallizations. In $CDCl_3$ one diastereomer exhibited the ethano methine proton resonance at 5.55 ppm while the second diastereomer's methine resonance appeared at 5.35 ppm; the respective melting points of the compounds are 199–202 °C and 140–143 °C. Employing the arguments advanced by Huang et al.,[16,17] the higher melting diastereomer is tentatively assigned the *meso* configuration.[18]

If polar interactions were to govern the conformations of *meso*-**5**, it would be expected that the preferred conformation of *meso*-**5** would be **5a** (Figure 1); there exists in this conformation two pairs of attractive interactions (pentafluorophenyl–*p*-methoxyphenyl), while in conformers **5b** and **5c** two pairs of repulsive interactions exist with only a single attractive interaction. For *dl*-**5**, conformer **5a** exhibits two pairs of repulsive interactions while both **5b** and **5c** exhibit two attractive and one repulsive interaction each. Assuming that the repulsive interaction between pentafluorophenyl groups would exceed that of *p*-methoxyphenyl groups, the preferred conformer of *dl*-**5** would be **5c**.

Nuclear magnetic resonance analysis of the two diastereomers was conducted at 300 MHz employing the ^{13}C satellite method.[3] In CCl_4 solution the 5.55 ppm diastereomer (*meso*) has $^3J_{HH} = 13.25 \pm 0.15$ Hz while the 5.35-ppm diastereomer (*dl*) has $^3J_{HH} = 12.65 \pm 0.05$ Hz. It is clear that both diastereomers exist predominantly in the H–H anti conformation and that the anticipated ring–ring interactions do not, in this case, overcome the repulsive steric interactions encountered in H–H gauche conformations. It should be noted, however, that the coupling constants observed are in agreement with the tentative configurational assignments, i.e., the *meso* diastereomer should prefer the H–H anti conformation to a greater extent than the *dl* diastereomer with a resultant greater vicinal coupling constant.

Experimental Section

(Pentafluorophenyl)(*p*-methoxyphenyl)methanol was prepared by the addition of 5.44 g (0.04 mol) of *p*-anisaldehyde to the Grignard reagent prepared from 12.35 g (0.05 mol) of bromopentafluorobenzene and 1.22 g (0.05 mol) of Mg turnings in 70 mL of anhydrous ether. Stirring was continued for 2 h after the addition was completed. The reaction mixture was cooled in an ice bath and the reaction was quenched with 10% aqueous HCl. The ether layer was separated and dried over anhydrous sodium sulfate. Removal of the ether under reduced pressure followed by distillation of the crude product at 141–143 °C at 0.4 mm afforded 7.9 g (65%) of the alcohol: ^1H NMR ($CDCl_3$) methine, δ 6.2; OCH_3, 3.8; aromatic, AA′BB′ quartet centered at 7.1.

***meso*- and *dl*-1,2-Bis(pentafluorophenyl)-1,2-bis(*p*-methoxyphenyl)ethane** were prepared by a method analogous to that reported by Finocchiaro et al.[15] for similar compounds. (Pentafluorophenyl)(*p*-methoxyphenyl)methanol (7.4 g, 0.024 mol) was dissolved in a mixture of 100 mL of acetone and 50 mL of concentrated hydrochloric acid. The solution was flushed with nitrogen and 8.43 g (0.068 mol) of chromium(II) chloride was added. The resultant reaction mixture was stirred under nitrogen for 3 h at room temperature. The suspension was filtered and the precipitate was washed with several portions of water. The precipitate was extracted with ether, the ether layer dried over anhydrous sodium sulfate was filtered, and the solvent was removed. ^1H NMR analysis ($CDCl_3$) indicated a 50:50 mixture of diastereomers. Recrystallization of the crude solid from hexane afforded two fractions: fraction 1, δ(methine) 5.55 ppm, mp 199–202 °C; fraction 2, δ(methine) 5.35 ppm, mp 140–143 °C. Anal. (Fraction 1). Calcd C, 58.45; H, 2.79. Found: C, 58.48; H, 2.92.

Registry No. *meso*-**5**, 95216-89-0; *dl*-**5**, 95216-90-3; (pentafluorophenyl)(*p*-methoxyphenyl)methanol, 95216-88-9; *p*-anisaldehyde, 123-11-5; bromopentafluorobenzene, 344-04-7.

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[15] The coupling reaction is analogous to one reported previously by Finnoccharo et al. (Finnaccharìo, P.; Gust, G.; Hounshell, W. D.; Hummel, J.; Maravigna, P.; Mislow, K. *J. Am. Chem. Soc.* **1976**, *98*, 4945).

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[18] See, however, the caveat and exception listed in ref 8.

Attractive Nonbonded Interactions. The Solution Conformation of *N*-(1-Phenyl-2-propyl)nicotinamide Chloride

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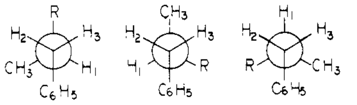
We[1] and others[2] have determined the solution conformation of 1,2-diphenylpropane. The predominant conformation in solution is, as expected on the basis of repulsive nonbonded interactions between contiguous phenyl groups, phenyl–phenyl anti (**1a**; R = C_6H_5). Similarly, we[3]



and others[4-6] have determined that amphetamine (**1**; R = NH_2) and its hydrochloride (**1**; R = $NH_3^+Cl^-$) prefer the phenyl–amino gauche, phenyl–methyl anti conformation (**1b**, R = NH_2 or $NH_3^+Cl^-$) in aqueous solution. As an extension of this work, investigation of a corresponding pyridinium salt (**2**) was undertaken. Comparison of 1,2-

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[6] Reference 5 purports that their results, "allowed us to correct previously made assignments." The correction had previously been made in ref 3, uncited in ref 5.