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CONFORMATIONAL ANALYSIS OF TETRAARYLETHANES

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Abstract—NMR evidence establishes that both diastereomers of 1,2-diphenyl-1,2-bis(4-pyridyl)ethane (**2**), identified by optical resolution of the racemic form, exist predominantly in the *anti* conformation. Furthermore, empirical force field calculations show that the *gauche* conformer of 1,1,2,2-tetrakis(2,6-dimethylphenyl)ethane (**3**) is less stable by *ca.* 10 kcal/mol than the *anti* structure. It thus appears that neither polar effects nor steric congestion are effective in reversing the marked preference of 1,1,2,2-tetraphenylethane (**1**) and other unclamped tetraarylethanes for an *anti* ground state. In contrast, as predicted by empirical force field calculations and confirmed by X-ray and NMR evidence, the ground state structure of 9,9'-bifluorenyl (**4**) is *gauche*. The conformational behavior of **1**–**4** is discussed in terms of the intramolecular aryl ring stacking in clamped and unclamped tetraarylethanes.

In contrast to 1,1,2,2-tetraalkylethanes, which prefer the *gauche* conformation,[1] 1,1,2,2-tetraphenylethane (**1**) has an *anti* ground state (**1a**),[2] and the *gauche* conformer (**1g**) is calculated to be *ca.* 5 kcal/mol less stable than **1a**.[3] How general is this preference among 1,1,2,2-tetraarylethanes? The present study was undertaken in order to answer this question, by testing the effect of polar and steric factors on the relative stability of *anti* and *gauche* forms in this class of compounds.

Polar effects

In previous studies of *meso*- and DL-1,2-diaryl-1,2-diphenylethanes, Huang *et al.* had shown[4,5] that the dipole moments of the diastereomers differ characteristically, the moments of the lower melting forms uniformly exceeding those of the higher melting ones. The largest such difference was observed[4] for the case of 1,2-diphenyl-1,2-bis(4-pyridyl)ethane (**2**), with reported dipole moments of 0.8 ± 0.1 and 4.1 ± 0.7 D for the higher and lower melting forms, respectively. In a closely reasoned analysis, Huang *et al.* argued[4,5] that these observations could be rationalized on the basis of two interlocking assumptions: that the higher and lower melting forms correspond to the *meso* and DL isomers, respectively, and that both diastereomers exist predominantly in the *anti* (with respect to the H's) conformation.

However, Huang's observations can also be rationalized if both sets of assignments are reversed, i.e. on the basis of the alternative set of assumptions that the higher and lower melting forms correspond to the DL and *meso* isomers, respectively, and that both diastereomers exist predominantly in a *gauche* (with respect to the H's) conformation. There exists no independent evidence which would allow a decision between these alternatives, and the m.p. criterion employed by Huang is unfortunately not infallible. For example, the isomers of 1,2-bis(2,6-dimethylphenyl)-1,2-di-t-butylethane with m.p. 216–218° and 224–226° correspond to the *meso* and DL forms, respectively,[6] and this configurational assignment has been confirmed by empirical force field (EFF) calculations[7] which match reported[6] NMR data. We therefore saw the need for more reliable stereochemical assignments, particularly in the case of **2** which is sterically very similar to **1**, but which differs appreciably from **1** in polarity.

Although the desired differentiation between *meso* and DL isomers is in principle easily carried out with chiral auxiliary agents,[8] preliminary experiments with **2** using chiral shift reagents gave no indication of resonance doubling, and we therefore resorted to the conventional technique of optical resolution. The higher and lower melting diastereomers of **2**, m.p. 267–270° and 226–229°, were separated as described.[4] The diastereomeric salts formed by the lower melting form with (+)-camphor-10-sulfonic acid were separated by fractional crystallization from ethanol and decomposed to yield the enantiomers of **2**, $[\alpha]_D -9.02°$ (CHCl$_3$) and $[\alpha]_D +9.40°$ (CHCl$_3$). Conclusive evidence was thus provided that the lower melting form of **2** has the DL configuration, in agreement with the earlier assignment.[4] Furthermore, the appreciable solubility of both diastereomers of **2** in CDCl$_3$ made possible a reliable analysis of the ^{13}C satellite lines of the methine proton signals (*meso* δ 4.67; DL δ 4.75) in the ^{1}H NMR spectra of both compounds. The coupling constants $^3J_{HH}$ of 12.5 and 13.0 Hz found for the DL and *meso* isomer, respectively, are consistent with a predominance of the *anti* conformation in both isomers,[9] in agreement with the earlier, more tentative, conclusion.[4]

For the DL isomer of **2**, the molecular moment would be considerably reduced if the operation of an intramolecular dipole effect were to lead to repulsion between the strongly polar 4-pyridyl groups, and hence to a conformation in which these groups are *anti*. Such a conformation would necessarily have the H's *gauche* to one another, contrary to observation. Conformational preferences in **2** are therefore dictated by the same factors which lead to a predominance of the *anti* form in **1**, and it thus appears that the conformational equilibria in these and similar tetraarylethanes are primarily determined by steric effects.

Steric effects

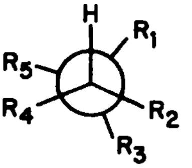
Whereas the conformer distribution in 1,1,2,2-tetramethylethane slightly favors the *gauche* form, in 1,1,2,2-tetra-t-butylethane the "*gauche*" form† is effectively the *only* conformer present.[1] This result is in agreement with EFF calculations,[10] which indicate that the *anti* form of tetra-t-butylethane lies 40 kcal/mol above the ground state. It therefore became of interest to investigate the effect of intramolecular crowding on the conformational equilibrium of 1 since, by analogy with the tetraalkyl systems, one might anticipate a narrowing of the *gauche-anti* energy gap, or possibly even a reversal in relative stability of *gauche* and *anti* forms.

Previous EFF calculations[4] on 1,1,2,2-tetrakis(2,6-dimethylphenyl)ethane (3), an overcrowded analog of 1, had led to an *anti* structure, in harmony with the X-ray structure (also *anti*) of the closely related 1,1,2,2-tetramesitylethane.[11] However, in the earlier study[3] no attempt had been made to search for a *gauche* energy minimum, on the unproven assumption that the *anti* conformation represented the ground state of the molecule. We therefore performed a more extensive search of the conformational hypersurface in order to locate any minima corresponding to *gauche* structures of 3, using a force field[12] which had previously been employed with success in studies of polyarylmethanes[12,13] and polyarylethanes.[3,14] Input structures were relaxed using the pattern search minimization technique with an energy criterion of 0.01 kcal/mol over one iteration. The full relaxation method was used, and structures were optimized without symmetry constraints.

Our search uncovered, in addition to the already established[3] *anti* form (3a), two *gauche* forms, $3g_1$ and $3g_2$, 11.2 and 9.5 kcal/mol less stable than 3a, respectively. These results clearly show that contrary to naive expectation, increasing the internal strain in an unclamped[14] tetraarylethane leads to *destabilization* of the *gauche* relative to the *anti* form, in contrast to what is observed for tetraalkylethanes. That is, an increase in the steric requirements of an aryl substituent has consequences opposite to those which accompany a corresponding increase in an alkyl substituent.

In tetraalkylethanes, particularly those with bulky alkyl (R) groups, geminal repulsions give rise to a severe spreading of the R–C–R bond angles. This deformation

Table 1. Calculated conformations of tetraarylethanes



Compd.	Point Group	Symmetry Equiv. R's[a]	ϕ_r[b] (deg)	ϕ_c[c] (deg)
1a[d]	C_2	$R_1 = R_2 = Ph$ $R_4 = R_5 = Ph$ $R_3 = H$	-74.8, -72.6 29.9, 29.7	61.8, -53.2, 61.4, -70.1, 43.1, -70.4
1g[d]	C_2	$R_2 = R_5 = Ph$ $R_3 = R_4 = Ph$ $R_1 = H$	-38.9, -38.5 72.2, 71.2	85.4, -24.5, 92.9, -39.9, 93.0, -24.3
3a[d]	C_2	$R_1 = R_2 = Xy$ $R_4 = R_5 = Xy$ $R_3 = H$	81.5, 81.7 33.9, 33.2	66.8, -40.0, 66.8, -82.6, 21.1, -82.7
$3g_1$	C_2	$R_2 = R_5 = Xy$ $R_3 = R_4 = Xy$ $R_1 = H$	55.7, 55.1 47.2, 46.3	1.8, -96.6, 1.3, -162.3, 1.8, -96.1
$3g_2$	C_1	$R_1 = Xy$ $R_2 = Xy$ $R_3 = Xy$ $R_4 = Xy$ $R_5 = H$	40.1 -41.0 64.1 -67.1	6.6, -86.5, 78.7, -83.6, 17.4, -87.3

[a] Xy = 2,6-dimethylphenyl. [b] The sign of the C_{ortho}-C_{aryl}-C_{ethane}-C_{ethane} dihedral angle ϕ_r is taken to be positive if, looking down the C_{aryl}-C_{ethane} bond, a counterclockwise rotation of the C_{aryl}-C_{ethane}-C_{ethane} plane eclipses the C_{ortho}-C_{aryl} and C_{ethane}-C_{ethane} bonds; the dihedral angle is 0° for the eclipsed conformation. [c] R(H)-C_{ethane}-C_{ethane}-R dihedral angles listed in the order: H-R_1, R_1-R_2, R_2-R_3, R_3-R_4, R_4-R_5, R_5-H. [d] Reference 3.

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†Since the ground state structure of 1,1,2,2-tetra-t-butylethane is so severely distorted that the Newman projection no longer displays a regular alternation of front and back substituents, the term "*gauche*" is not strictly applicable.[7]

causes an increase in destabilizing vicinal repulsions for the *anti* conformer but not for the *gauche*, and the latter therefore emerges as the ground state.[1] The underlying reason for the dramatic reversal in conformational preference on going to the tetraarylethanes can be traced to the ability of neighboring aryl rings to nest or stack.[2] This stacking greatly diminishes geminal repulsions and the valence angle spread which results from them. The conformational preference of unclamped tetraarylethanes is thus determined by a minimization of vicinal interactions, which leads to an *anti* preference for conventional reasons. That the destabilization of **3g** relative to **3a** (by *ca.* 10 kcal/mol) is significantly greater than that of **1g** relative of **1a** (by *ca.* 5 kcal/mol) is understandable in terms of the unavoidable compression of Me groups brought into close proximity by the vicinal xylyl groups in **3g**.

Evidence for intramolecular stacking in **3g** derives from an analysis of the structural information provided by the EFF output (Table 1). It had previously been noted[14] that the nearly eclipsed D_3 conformation of hexaphenylethane results from the optimal nesting of the two homochiral trityl moieties. Just such an effect is also exhibited by **3g**$_1$. Unlike **1g**, which it resembles only in overall symmetry (C_2), **3g**$_1$ is nearly eclipsed (three ϕ_c's are nearly 0°) and all four ring dihedral angles (ϕ_r) are of the same sign, corresponding to homochiral propeller moieties. This remarkable resemblance of **3g**$_1$ to D_3-hexaphenylethane is complemented by a similar resemblance between the other *gauche* form, **3g**$_2$, and S_6-hexaphenylethane;[14] now the ϕ_r's have oppositely signed values for the two ends of the molecule (Table 1), corresponding to heterochiral propeller moieties.

It thus appears that neither polar not steric effects are capable of reversing the strong preference of unclamped tetraarylethanes for the *anti* conformation. A very different situation exists for doubly back clamped polyarylethanes containing two fluorenyl moieties, such as 9,9'-bifluorenyl (**4**), 9,9'-diphenyl-(9,9')-bifluorenyl, and bifluoradenyl: in each of these compounds, the *anti* form is calculated to be *less* stable than the *gauche* ground state.[14] This contrast in the conformational behavior of clamped and unclamped polyarylethanes seemed of sufficient interest to warrant further examination. In particular, although indirect experimental support was available in the observation that 10,10'-dianthronyl is *gauche* both in the crystalline state[15] and in solution,[16] no experimental evidence appeared to exist which would bear directly on the conformational preference of any bifluorenyl. We therefore subjected our computational conclusions to an experimental test. Our system of choice was **4**, whose *gauche* ground state structure, according to our calculations,[14] is 6.6 kcal/mol more stable than the *anti* conformer.

The crystal and molecular structure of **4** was determined by X-ray diffraction. Crystals of **4**, obtained from acetone, were monoclinic, space group $P2_1/n$, with $a = 17.586(2)$, $b = 17.764(3)$, $c = 5.682(1)$ Å, $\beta = 91.44(1)°$ and $Z = 4$. A crystal measuring approximately $0.1 \times 0.2 \times 0.6$ mm was used for the analysis (Hilger–Watts four-circle diffractometer, Ni-filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). Of the 2384 independent reflections for $\theta < 57°$, 1874 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple solution procedure[17] and was refined by full matrix least squares. In the final refinement, anisotropic thermal parameters were used for the C atoms and isotropic temperature factors were used for the H atoms. The H atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are $R = 0.041$ and $wR = 0.042$ for the 1874 observed reflections. The final difference map has no peaks greater than ±0.1 e Å. Estimated standard deviations are ±0.003 Å for C–C bonds and ±0.2° for C–C–C angles. A stereoview of the final structure of **4** is given in Fig. 1, and the final parameters in Tables 2 and 3.

It is evident from Fig. 1 that the conformation of **4** in the crystal is *gauche* and has C_2 symmetry, in accord with prediction.[14] Table 4 gives a comparison of calculated (EFF) and experimentally determined (X-ray) structural parameters. As in similar, previously reported comparisons,[2,13b] overall agreement is excellent. However, contrary to expectations,[14] the experimentally found central C1–C2 bond distance is not significantly larger than that calculated by the EFF method.

Evidence that the *gauche* conformation of **4** also predominates in solution was provided by NMR coupling constant data. The low solubility of **4** in common NMR solvents prevented a reliable analysis of the ^{13}C satellite lines using material of natural isotopic composition, as described for the case of **2**. This difficulty was overcome by measuring $^3J_{HH}$ directly on a sample of [9-^{12}C]-9,9'-bifluorenyl, prepared by coupling [9-^{13}C]fluorenone with

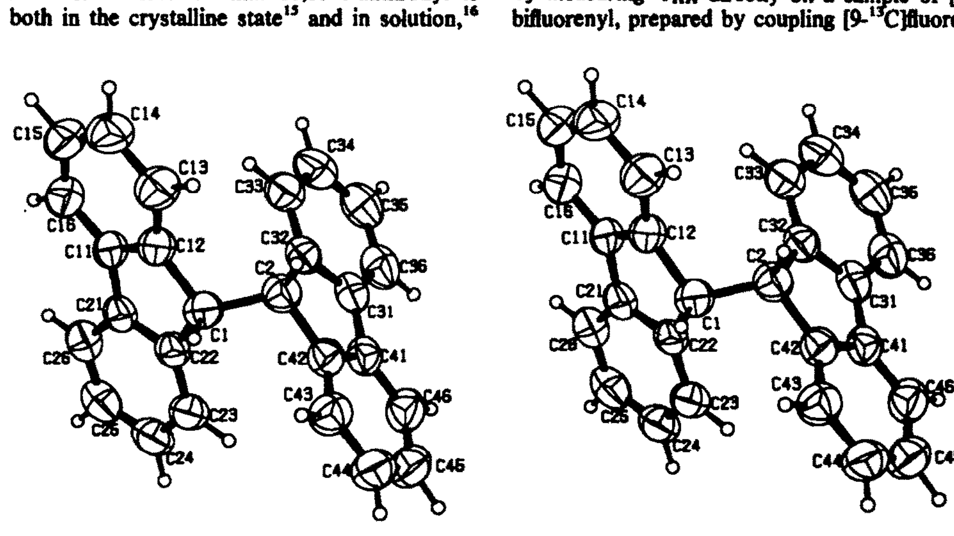

Fig. 1. Stereoview of the X-ray structure of 4.

Table 2. Final atomic parameters for 4 with standard deviations in parentheses

Atom	x	y	z	B
C(1)	0.58348(12)	0.73852(11)	0.4818(3)	*
C(2)	0.49592(12)	0.73424(11)	0.4806(4)	*
C(11)	0.66945(11)	0.65969(12)	0.2777(4)	*
C(12)	0.62171(12)	0.66234(11)	0.4684(4)	*
C(13)	0.61405(14)	0.60050(14)	0.6135(4)	*
C(14)	0.65434(16)	0.53531(14)	0.5613(5)	*
C(15)	0.70077(15)	0.53218(14)	0.3708(6)	*
C(16)	0.70914(13)	0.59409(14)	0.2263(5)	*
C(21)	0.66917(11)	0.73323(12)	0.1619(4)	*
C(22)	0.61855(11)	0.78026(11)	0.2787(4)	*
C(23)	0.61023(13)	0.85461(12)	0.2092(4)	*
C(24)	0.65223(14)	0.88121(13)	0.0240(5)	*
C(25)	0.70275(14)	0.83488(15)	-0.0902(4)	*
C(26)	0.71176(12)	0.76018(14)	-0.0230(4)	*
C(31)	0.40572(11)	0.75238(12)	0.1642(4)	*
C(32)	0.45699(11)	0.70063(12)	0.2635(4)	*
C(33)	0.46278(13)	0.62880(12)	0.1704(4)	*
C(34)	0.41632(15)	0.60935(14)	-0.0229(4)	*
C(35)	0.36517(14)	0.66078(16)	-0.1189(4)	*
C(36)	0.35958(13)	0.73253(15)	-0.0273(4)	*
C(41)	0.40869(11)	0.82202(12)	0.3024(4)	*
C(42)	0.45918(12)	0.81118(12)	0.4928(4)	*
C(43)	0.47059(13)	0.86734(13)	0.6587(4)	*
C(44)	0.43283(15)	0.93510(13)	0.6286(5)	*
C(45)	0.38443(15)	0.94648(14)	0.4374(5)	*
C(46)	0.37121(13)	0.89051(14)	0.2725(5)	*
H(1)	0.6013	0.7641	0.635	5.0
H(2)	0.4797	0.7036	0.624	5.0
H(13)	0.5799	0.6034	0.759	7.0
H(14)	0.6492	0.4889	0.668	8.0
H(15)	0.7299	0.4836	0.330	8.0
H(16)	0.7427	0.5921	0.081	7.0
H(23)	0.5737	0.8902	0.297	6.0
H(24)	0.6465	0.9356	-0.029	7.0
H(25)	0.7330	0.8566	-0.225	7.0
H(26)	0.7484	0.7253	-0.110	7.0
H(33)	0.5002	0.5915	0.246	6.0
H(34)	0.4209	0.5562	-0.094	7.0
H(35)	0.3309	0.6447	-0.260	7.0
H(36)	0.3226	0.7711	-0.099	7.0
H(43)	0.5065	0.8580	0.803	6.0
H(44)	0.4390	0.9768	0.753	7.0
H(45)	0.3589	0.9979	0.413	7.0
H(46)	0.3351	0.8990	0.131	7.0

*Anisotropic thermal parameters are given in Table 3.

Table 3. Final anisotropic thermal parameters for 4 with standard deviations in parentheses

Atom	B11x10^5	B22x10^5	B33x10^4	B12x10^5	B13x10^4	B23x10^4
C(1)	369(9)	333(8)	337(8)	9(7)	-18(2)	0(2)
C(2)	368(9)	344(8)	343(8)	-5(7)	0(2)	10(2)
C(11)	295(8)	326(9)	414(9)	12(7)	-28(2)	-3(2)
C(12)	338(8)	339(9)	379(9)	4(7)	-23(2)	7(2)
C(13)	491(11)	420(10)	485(11)	26(9)	-20(3)	34(3)
C(14)	530(12)	376(10)	673(14)	-12(9)	-43(3)	42(3)
C(15)	443(11)	366(10)	738(15)	56(8)	-37(3)	-3(3)
C(16)	377(9)	411(10)	560(11)	41(8)	-14(3)	-9(3)
C(21)	283(8)	368(9)	372(9)	-33(7)	-19(2)	-3(2)
C(22)	290(8)	324(8)	368(9)	-30(6)	-24(2)	2(2)
C(23)	397(9)	328(9)	472(10)	-37(7)	-15(3)	9(2)
C(24)	433(10)	380(9)	541(11)	-89(9)	-23(3)	24(3)
C(25)	408(10)	529(12)	450(11)	-131(9)	-6(3)	27(3)
C(26)	342(9)	481(11)	447(10)	-43(8)	-2(2)	-5(3)
C(31)	279(8)	426(9)	366(8)	-37(7)	4(2)	13(2)
C(32)	308(8)	354(8)	364(9)	-47(7)	6(2)	8(2)
C(33)	405(9)	392(10)	461(10)	-47(8)	-3(3)	3(3)
C(34)	486(11)	457(11)	484(11)	-138(9)	-1(3)	-18(3)
C(35)	434(11)	605(13)	459(11)	-122(10)	-23(3)	-5(3)
C(36)	371(10)	540(12)	458(10)	-47(9)	-13(3)	15(3)
C(41)	292(8)	396(9)	380(9)	-1(7)	17(2)	20(2)
C(42)	335(8)	356(9)	361(9)	-9(7)	16(2)	9(2)
C(43)	463(10)	412(10)	415(10)	14(8)	11(3)	-3(3)
C(44)	535(12)	378(10)	542(12)	12(9)	42(3)	-7(3)
C(45)	500(12)	391(11)	628(13)	73(9)	48(3)	25(3)
C(46)	392(10)	456(11)	507(11)	52(8)	10(3)	29(3)

The anisotropic temperature factor has the form

$$\exp(-(\underline{h}^2 B11 + \underline{k}^2 B22 + \underline{l}^2 B33 + 2\underline{hk}B12 + 2\underline{hl}B13 + 2\underline{kl}B23)).$$

Table 4. Calculated (EFF) and experimental (X-Ray) structural parameters for 4

Atomic Parameters [a]	EFF	X-Ray
	Bond Lengths (Å)	
C1-C2	1.543	1.542
C1-C12	1.513	1.514
C1-C22	1.519	1.516
C11-C21	1.463	1.463
C_{aryl}-C_{aryl} [b]	1.392	1.387
	Bond Angles (deg)	
C2-C1-C12	113.0	113.6
C2-C1-C22	115.2	116.5
C12-C1-C22	100.1	102.1
C1-C12-C11	111.8	110.4
C1-C12-C13	127.2	129.1
C11-C12-C13	121.0	120.5
C1-C22-C21	111.4	110.1
C1-C22-C23	128.2	129.9
C21-C22-C23	120.3	119.9
C12-C11-C16	120.5	120.6
C12-C11-C21	108.0	109.0
C16-C11-C21	131.5	130.4
C11-C21-C22	108.2	108.4
C11-C21-C26	130.9	130.7
C22-C21-C26	120.9	120.8
	Dihedral Angles (deg)[c]	
C2-C1-C12-C13	-62.2	-55.7
C2-C1-C22-C23	64.3	60.4
C12-C1-C2-C32	-69.6	-62.1
C12-C1-C2-C42	176.2	-179.7
C22-C1-C2-C32	44.6	56.2
C22-C1-C2-C42	-69.6	-61.4
H1-C1-C2-H2	-65.8	-59.7[d]
H1-C1-C2-C42	55.1	60.4[d]

[a] Atom designations correspond to those given in Figure 1. [b] Values are given for the average of the 24 benzene bond lengths. For the EFF calculation, the standard deviation from the mean is ±0.002Å. [c] See Table 1, footnote b. [d] Hydrogen atoms were not refined.

lithium 9-fluorenyl and reduction of the resulting [9-^{13}C]-9-hydroxy-9-fluorenylfluorene. The ^{1}H NMR spectrum of the ^{13}C-labeled 4 displayed the expected lines of the AB portion (methine protons) of an ABX spin system. The value of $^3J_{HH}$ thus found, 4 Hz, is consistent with the *gauche* conformation.[9] Furthermore, this value remained invariant up to 155°C (in 1,2,4-trichlorobenzene) in accord with the predicted[14] strong preference of 4 for the *gauche* structure.

The rationale for the reversal in conformer preference is not difficult to discern. As revealed most simply by inspection of molecular models, and as borne out by the detailed output of the EFF calculations, back clamping disallows aryl ring stacking. In the anti conformation the hydrogens on the 1,8-positions of one fluorenyl moiety are forced to point directly at their counterparts, i.e. at the hydrogens on the 1′,8′-positions of the other fluorenyl moiety. These severe H···H nonbonded interactions are greatly relieved in the *gauche* conformation.

The conformational reversal exhibited by 4 and similar molecules relative to 1–3 thus provides strong supporting evidence for the aryl stacking model invoked to rationalize the anti preference uniformly exhibited by unclamped tetraarylethanes.

To complete our analysis of the effect of back clamping on conformational equilibria, we performed EFF calculations on the singly back clamped tetraarylethane 9-benzhydrylfluorene (5). This molecule may be regarded as a hybrid of unclamped 1 and doubly back clamped 4. Our calculations uncovered a *gauche* and an *anti* minimum, with the *anti* form slightly more stable (by 0.6 kcal/mol) than the *gauche*. The progression of energy differences 1 (g − a) = 5 kcal/mol, 5 (g − a) = 0.6 kcal/mol, and 4 (g − a) = −6.6 kcal/mol provides strong evidence that a single back clamp is roughly half as effective as two in stabilizing the *gauche* relative to the *anti* form.

EXPERIMENTAL

^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian A-60A or XL-100 instrument. Optical rotations were measured on a Perkin-Elmer model 141 polarimeter (*c* is reported as g per 100 ml). M.ps were determined on a Thomas–Hoover apparatus and are corrected.

Resolution of DL ***- 1,2 - diphenyl - 1,2 - bis(4 - pyridyl)ethane* (2).** The diastereomeric 1,2 - diphenyl - 1,2 - bis(4 - pyridyl)ethanes were prepared and separated into *meso* and DL forms as previously described.[18] In contrast to the higher melting isomer (m.p. 267–270°; lit.[18] m.p. 267–268°), which formed a crystalline tartrate (m.p. 191.5–194.5°) with (+)-tartaric acid, we were unable to obtain a crystalline tartrate of the lower melting isomer (m.p. 226–229°; lit.[18] m.p. 226–227°).

In preliminary experiments designed to select a suitable acid for the resolution of 2, salts of the lower melting isomer with (+)-camphor-10-sulfonic, (+)-mandelic, (+)-camphoric, and (−)-malic acids were prepared in acetone, chloroform, ethanol, and methanol solutions. Crystals were obtained with (+)-camphor-10-sulfonic acid in ethanol and with (+)-camphoric acid in methanol.

Since the crystals with (+)-camphor-10-sulfonic acid appeared to be better developed, this system was our first choice for the resolution. A soln of 0.48 g (1.43 mmol) of the lower melting isomer of 2 and 0.33 g (1.44 mmol) of (+)-camphor-10-sulfonic acid deposited white crystals (0.36 g, m.p. 195–288°) after 5 hr at room temp. Tow recrystallizations from ethanol gave 0.12 g of white crystals, m.p. > 300° (dec). The base was liberated from this head fraction on treatment with Na$_2$CO$_3$ aq and was extracted into chloroform. Evaporation of the solvent under reduced pressure yielded 0.068 g of white solid, m.p. 232–236°, $[\alpha]_D^{31} - 9.02°$ (*c* 2.03), CHCl$_3$). (Found: C, 85.74; H, 6.21. Calc. for C$_{24}$H$_{20}$N$_2$: C, 85.68; H, 5.99%).

The mother liquors were collected and subjected to further fractional crystallizations. The base liberated from the mother liquor of the tail fraction was treated with sat Na$_2$CO$_3$, and then extracted with CHCl$_3$. The CHCl$_3$ layer was washed with water, dried (Na$_2$SO$_4$) and the solvent was removed under reduced pressure to give 0.048 g of white solid (m.p. 226–232°), $[\alpha]_D^{31} + 9.40°$ (*c*, 2.41, CHCl$_3$).

[9-^{13}C]-9-*Hydroxy-9-fluorenylfluorene*. A soln of 2.29 M BuLi (*ca.* 1.4 ml) was added to a soln of 0.53 g of fluorene in 10 ml of ether. [9-^{13}C]Fluorenone (0.57 g, MS & D, 90% enriched) in 25 ml of ether was then added dropwise to the yellow-orange solution. After 2 hr of stirring at room temp., the mixture was quenched with 15 ml of a sat NH$_4$Cl aq. The two phases were separated, the aqueous layer was extracted twice with 20 ml ether, and the ether extracts were combined with the original organic layer. The combined organic phase was washed with water, dried over Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The resulting orange oil gave, after trituration with 30–60° petroleum ether, 0.45 g (42%) of crude product, m.p. 180–194° (lit.[19] m.p. 195°).

[9-^{13}C]-9,9′-*Bifluorenyl*. HI (48%, 8 ml) was added dropwise to a suspension of 0.45 g of [9 - ^{13}C] - 9 - hydroxy - 9 - fluorenylfluorene in 4 ml AcOH and 4 ml Ac$_2$C. The mixture darkened, and heat was evolved. Stirring was continued for 2 hr at room temp. The mixture was then poured into 40 ml water, and the orange-brown ppt was filtered off and recrystallized from ethanol-toluene (2:1) to give 0.40 g (93%) of pale yellow crystals, m.p. 244–246° (lit.[20] m.p. 246°). The ^{1}H NMR spectrum in the methine proton region displayed a set of doublets ($^3J_{HH}$ 4 Hz) centered about δ 4.83 (lit.[21] δ 4.71 for unlabeled 4), and separated by $^1J_{CH}$ 133 Hz.

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