

Tetraalkyldisilanes as Models for the Conformational Analysis of Tetraalkyldiphosphines

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Abstract: The remarkable similarity in the static and dynamic stereochemistry of tetraalkyldisilanes and the corresponding diphosphines, as revealed through a study of 1,1,2,2-tetramethyl-, tetra-*tert*-butyl-, and tetracyclohexyldisilane by dynamic NMR spectroscopy, X-ray crystallography, and empirical force field calculations, indicates that an electronic "gauche effect" need not be invoked to explain the conformational behavior of tetraalkyldiphosphines with respect to rotation about the P-P bond.

The conformational preference of diphosphines for the gauche form is exhibited by diphosphine itself^{2,3} and by 1,1,2,2-tetraalkyldiphosphines, which are either mixtures of anti and gauche forms⁴ or are exclusively gauche.⁵⁻⁷ However, in contrast to the 1,1,2,2-tetraalkylethanes, whose similar bias for the gauche form⁸⁻¹⁰ is due to conventional steric factors, the origin of this preference in the diphosphines has been considered to be essentially electronic in nature, resulting from the interactions of adjacent lone pairs and polar bonds (the "gauche effect").¹¹

The similarity of Si-Si and P-P bond lengths (2.33 and 2.22 Å, respectively)^{2b} and of C-Si and C-P bond lengths (1.87 and 1.87 Å, respectively)¹² suggested to us that a conformational analysis of disilanes might prove useful in gauging the importance of the gauche effect in the corresponding diphosphines. That is, because of the similarity in the metric (steric) properties of the two classes (i.e., disilanes and diphosphines), and because conformational preferences in disilanes cannot reasonably be ascribed to "gauche effects", any significant conformational differences between analogous derivatives R₂HSi-SiHR₂ and R₂P-PR₂ might therefore be taken as manifestations of a nonsteric, i.e., electronic ("gauche"), effect in the diphosphines. Conversely, the absence of any such differences would indicate the unimportance of special electronic effects.¹³

For the purpose of such a study, we chose to investigate three tetraalkyldisilanes. Two of these, 1,1,2,2-tetramethyldisilane (**1**) and 1,1,2,2-tetra-*tert*-butyldisilane (**2**), represent two extremes in steric congestion brought about by alkyl substitution. The third, 1,1,2,2-tetracyclohexyldisilane (**3**), represents an intermediate case. Appropriate structural information being available for the corresponding diphosphines (as well as ethanes), the stage was set for the desired comparisons. In the following, each of the three systems will be separately discussed; the salient results of these studies are summarized in the concluding section.

1,1,2,2-Tetramethyldisilane (1). In calculating the ground-state structure of this compound (**1**) by the previously described¹⁵ empirical force field (EFF),¹⁶ we uncovered two minima, corresponding to a gauche form (**1g** or its enantiomer, **1ḡ**) and an anti form (**1a**), with the former 0.2 kcal/mol lower in steric energy. Such small energy differences are considered to be within the error limits of the method^{16a,17} and the two structures should be thought of as essentially equal in energy. That is, **1** exists as a nearly statistical mixture of gauche and anti conformers. Both **1g** (or **1ḡ**) and **1a** are essentially strain-free structures; nonbonded interactions of the attractive type are numerous as evidenced by the negative steric energies (Table I). Although the reliability of the nonbonded potential in the attractive region is relatively untested, the results of this

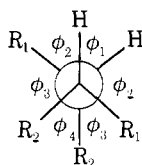
and previous studies^{15b,18} indicate that the present form produces reliable results.

Our conclusions receive support from the experimentally determined dipole moment (μ) of **1** in cyclohexane, 1.25 ± 0.02 D.¹⁹ Using the reported¹⁹ bond moments and the EFF structures, the dipole moments for **1g/1ḡ** and **1a** can be calculated, weighted according to the EFF energy difference, and appropriately summed to yield $\mu = 1.31$ D, in good agreement with experiment. Although it had previously been remarked¹⁹ that the experimental μ of **1** is in excellent agreement with the value of 1.25 D calculated¹⁹ on the basis of a free rotation model, it can be shown²⁰ that for any symmetrically substituted compound of the type R₂HM-MHR₂ (e.g., **1**) the μ calculated on the basis of this model is precisely the same as that calculated on the basis of a statistical (2:1) mixture of gauche and anti conformers.²²

Interconversion among the three conformers, **1g**, **1ḡ**, and **1a**, is conveniently analyzed by considering the process of enantiomerization, **1g** ⇌ **1ḡ**. Two distinct pathways may be envisaged. The molecule may twist directly from **1g** to **1ḡ** by eclipsing hydrogens in a gauche ⇌ gauche mechanism (G ⇌ G). Alternatively, the rotation may proceed through **1a** by a gauche ⇌ anti ⇌ gauche mechanism (G ⇌ A ⇌ G). This dichotomy of rotational pathways has previously been discussed for other, related systems.^{3,5a,8,9a} In the present case, the relative importance of the two pathways was roughly gauged from the computed relative steric energies of the idealized transition states. As a somewhat crude approximation, we represented the G ⇌ G and G ⇌ A transition states by freezing dihedral angles²³ ϕ_3 and ϕ_4 (Table I) at 0° and calculating the steric energies by the EFF method. Barrier heights of 0.97 and 1.34 kcal/mol were thus calculated for the G ⇌ G and G ⇌ A transition states, respectively. The two barriers are therefore the same within the error limits of the method.

It is instructive to compare the results obtained for **1** with the available information on the conformational behavior of tetramethylethane (2,3-dimethylbutane) and tetramethyldiphosphine. Tetramethylethane consists of a nearly statistical (2:1) mixture of gauche and anti conformers,⁹ and in tetramethyldiphosphine both gauche and anti forms are also significantly populated.⁴ The static behavior of **1** therefore fits into the pattern set by the two comparison compounds. The barrier for internal rotation in tetramethylethane, 4.3 ± 0.2 kcal/mol,^{9a} is substantially higher than that calculated for **1**, in harmony with the expectation that the separation of the two rotors by the longer central bond in the disilane should bring about a lowering of the transition state energy.

The upper limit of 7 kcal/mol found^{2a} for central bond rotation in tetramethyldiphosphine is consistent with our conjecture, based on the corresponding similarity between **2**

Table I. Structural Parameters of Gauche Tetraalkyldisilanes^a

compd	R	SE ^b	Si-Si	Si-R _n	Si-Si-R _n	Si-Si-H	φ _n	ψ _n ^c
1g ^d	Me	-4.59	2.338	1.870, 1.870	108.3, 107.9	110.1	58.7, -62.0, 58.1, -61.1	-59.7, -60.7
2g	<i>t</i> -Bu	0.85	2.391	1.899, 1.905	108.0, 119.1	103.8	94.7, -14.5, 97.6, -40.9	-53.4, -48.7
3g (EFF)	Cy	6.22	2.355	1.877, 1.881	108.2, 111.0	110.6	108.2, -8.8, 110.3, -13.5	(63.9, -60.0), ^e (-71.9, 165.0)
3g (X-ray) ^f	Cy		2.365	1.886, 1.885	110.5, 114.0	107.0	115.7, -1.4, 114.2, -13.0	(64.6, -60.5), ^e (-56.7, 179.0)

^a Subscripted parameters (Si-R_n, Si-Si-R_n, φ_n, ψ_n) are listed in numerical order. For example, for **2g**, Si-R₁ = 1.899, Si-R₂ = 1.905; φ₁ = 94.7, φ₂ = -14.5, φ₃ = 97.6, φ₄ = -40.9; ψ₁ = -53.4, ψ₂ = -48.7. Energies are given in kcal/mol, bond lengths in Å, bond and dihedral angles in deg. All structures have C₂ symmetry. ^b Total steric energy as defined in eq 1 of ref 15a. ^c The degree of twist of the appropriate R group. For **2g** and **3g** this corresponds to an Si-Si-C-C dihedral angle; for **1g** an Si-Si-C-H angle is given. ^d **1a** has virtual C_{2h} symmetry, with Si-Si = 2.338, Si-C = 1.870, Si-Si-C = 108.3, Si-Si-H = 110.7, and ψ ca. 60°. ^e Two values of ψ are given for each R in **3g** corresponding to the two different Si-Si-C-C angles for each group. ^f Note that since the H positions were not refined, parameters involving H are less reliable.

and tetra-*tert*-butyldiphosphine (see next section), that the internal rotation barrier in tetramethyldiphosphine is of the order of 1-2 kcal/mol.

1,1,2,2-Tetra-*tert*-butyldisilane (2). According to our EFF calculations,¹⁵ the gauche conformer (**2g**) is more stable than the anti form (**2a**) by 11.9 kcal/mol. In contrast to **1a** (virtual C_{2h} symmetry), **2a** is appreciably distorted (φ(H-Si-Si-H) = 153°) and chiral (C₂). Structural parameters for **2g** are given in Table I. At the slow exchange limit (below -30 °C), the ¹H NMR spectrum exhibits the two *tert*-butyl signals expected for **2g**, and there is no signal indicative of the presence of **2a**. The NMR spectrum is thus fully consistent with the conclusion drawn from the EFF calculation that only **2g** is significantly populated at ordinary temperatures.

The two *tert*-butyl signals coalesce at -15 °C; at that temperature, ΔG[‡] = 13.8 ± 0.3 kcal/mol.²⁴ To determine whether the G ⇌ G (i.e., **2g** ⇌ **2g**) or the G ⇌ A ⇌ G (i.e., **2g** ⇌ **2a** ⇌ **2a** ⇌ **2g**) mechanism is responsible for the observed site exchange, the torsional profile of **2** was calculated by the EFF method (Figure 1).²⁵⁻²⁷ The calculations predict barriers of 24.9 and 15.1 kcal/mol for the G ⇌ G and G ⇌ A ⇌ G mechanisms, respectively, and we thus conclude that the latter is responsible for the observed coalescence, as found for analogous systems.^{3,8,9a}

The gauche ground state adopted by **2**, and the sizable energy gap which separates it from the anti form, are features shared by the analogous diphosphine. The low-temperature NMR spectrum of tetra-*tert*-butyldiphosphine is consistent with exclusive population of the gauche conformer.⁵ By analogy with **2**, the observed⁵ coalescence phenomenon (ΔG[‡] = 12.6 ± 0.1 kcal/mol at -45 °C) may be ascribed to enantiomerization of the gauche diphosphine through rotation around the P-P bond by the G ⇌ A ⇌ G mechanism, as previously suggested.^{5a}

The structure of **2g** (Table I) stands in contrast to the highly distorted structure of tetra-*tert*-butylethane,²⁸ whose enantiomerization barrier is >23 kcal/mol.⁸

1,1,2,2-Tetracyclohexyldisilane (3). Unlike methyl or *tert*-butyl groups, cyclohexyl groups lack threefold symmetry. The conformational hypersurface of **3** is therefore much more complex than that of **1** or **2**. The orientation of a cyclohexyl ring can be unambiguously defined by the Si-Si-C-H dihedral angle (δ), for which three descriptors, +, -, and a (for anti), are applicable, depending on whether 0° < δ < 120°, -120°

< δ < 0°, or |δ| ≥ 120°, respectively. This scheme results in 45 gauche and 27 anti forms, assuming all cyclohexyl rings to be in the chair form and to be equatorially substituted.²⁹ Consideration of all these forms is infeasible, and a method of selecting the best input structures for the EFF study is necessary. In our experience with the EFF method we have found that the global minima³⁰ of appropriately substituted ethanes correspond to symmetric structures containing either a center of inversion or a twofold rotation axis. Accordingly, for our study of **3**, only symmetric input structures²⁹ were considered. This simplification leaves 9 C₂ gauche and 12 anti input structures (three each of C_{2h}, C_i, C_s, and C₂ symmetry). All other geometrical input parameters were standard.

Relaxation of the 21 input structures described above gave rise to 18 unique minima, depicted in Figure 2. The global minimum³⁰ is a gauche C₂ form (**3g**) but another C₂ gauche and a C_i anti form lie within only 1.2 kcal/mol, an energy difference close to the EFF error limits. The complexity of the EFF hypersurface made it essential to verify the above conclusions by an independent experimental method. The results are described in the following subsection.

X-ray Structure. Compound **3**, a previously unreported substance, was readily prepared by conventional means (Experimental Section). Crystals of **3**, obtained from pentane, are orthorhombic, space group P2₁2₁2₁, with *a* = 9.472 (2) Å, *b* = 12.906 (2) Å, *c* = 20.609 (3) Å, and *d*_{calcd} = 1.030 g cm⁻³ for *Z* = 4 (C₂₄H₄₆Si₂, mol wt 390.80). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ-2θ scans, pulse height discrimination). A crystal measuring approximately 0.20 × 0.25 × 0.5 mm was used for data collection; the data were corrected for absorption (μ = 12.5 cm⁻¹). A total of 1961 reflections were measured for θ < 57°, of which 1831 were considered to be observed (*I* > 2.5σ(*I*)). The structure was solved by Patterson and Fourier methods and was refined by full-matrix least squares. In the final refinement anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are *R* = 0.039 and *wR* = 0.050 for the 1831 observed reflections. The final difference map has no peaks greater than ±0.2 e Å⁻³. A stereoview of the final structure is given in Figure 3.

A comparison of the X-ray structure of **3** and the calculated

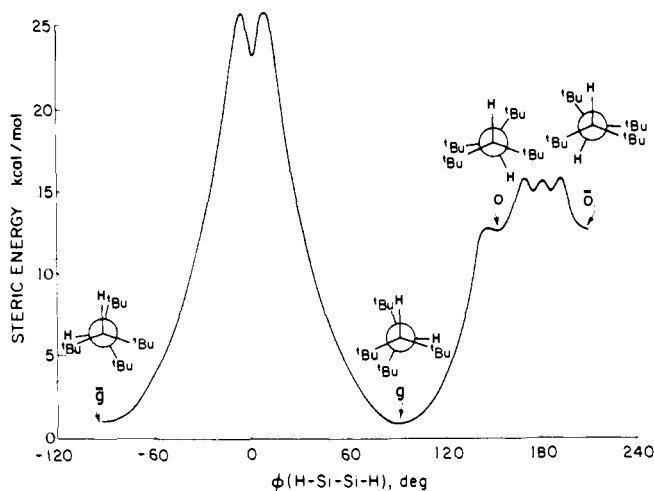


Figure 1. Calculated torsional profile of tetra-*tert*-butylsilane (**2**).

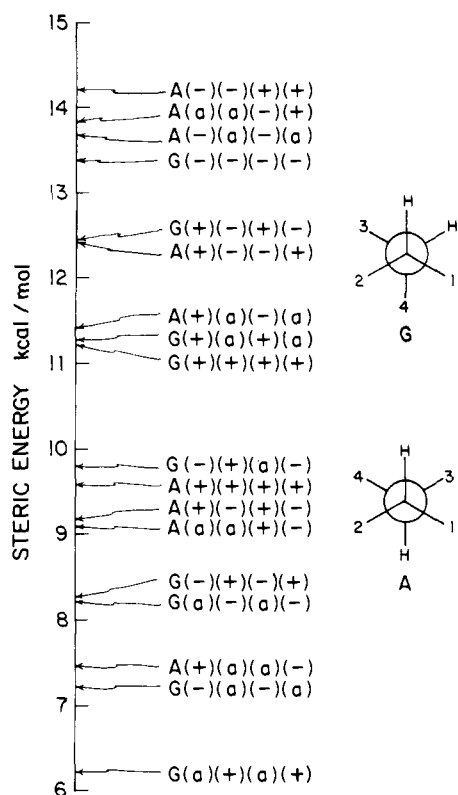


Figure 2. The 18 EFF minima for tetracyclohexyldisilane (**3**). The steric energy (ref 15a) for each form is indicated on the numbered scale. The four cyclohexyl ring twist descriptors (see text) are listed in numerical order according to the appropriate reference structure given on the right. For example, the lowest energy structure (SE = 6.22 kcal/mol) is gauche (G), and the appropriate ring twist descriptors for the groups in positions 1, 2, 3, and 4 of the G reference structure are a, +, a, and +, respectively.

minimum energy conformation (**3g**) may be made on the basis of the structural parameters given in Table I. Bond lengths and bond angles are in good agreement, and the overall shapes of the two structures, as indicated by ϕ and ψ , are the same. While such accord between EFF and X-ray structural parameters is not surprising,³¹ it is remarkable that the EFF succeeded in pinpointing the one correct ground-state conformation out of 18 minima. Incidentally, we note that the internal strain in **3g** is significantly less than in **2g**, as indicated by the C-Si-C bond angle of 112.4° (calculated) or 112° (X-ray) for the former and of 118.0° (calculated) for the latter.

A comparison of **3** with 1,1,2,2-tetracyclohexyldiphosphine

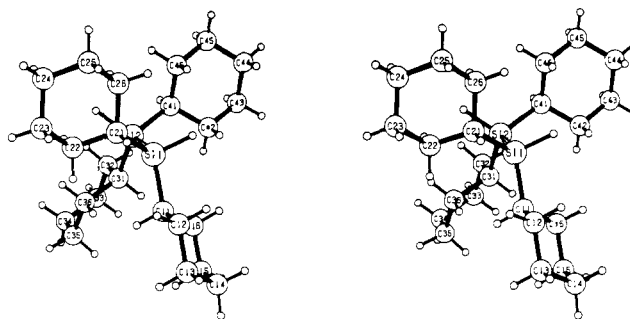


Figure 3. Stereoview of the X-ray structure of tetracyclohexyldisilane (**3**).

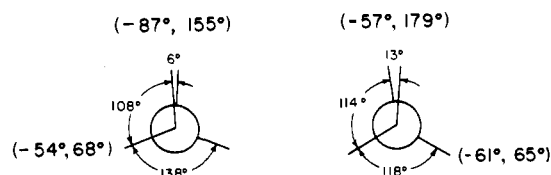


Figure 4. Newman projections of the X-ray structures of tetracyclohexyldiphosphine (**4**) (left, ref 6) and tetracyclohexyldisilane (**3**) (right). The projection is along the P-P (**4**) or Si-Si (**3**) bond. Numbers in parentheses give ring twist angles (ψ , see Table I). For symmetry equivalent angles (molecular C_2 symmetry) the average values are given. The Si-H bonds in **3** have been omitted.

(**4**)⁶ reveals a striking similarity in the structure of the two compounds (Figure 4). Both adopt a gauche C_2 conformation, with the cyclohexyl chairs linked to the heteroatoms by equatorial bonds. In both molecules, one pair of cyclohexyl groups is almost eclipsed, and corresponding cyclohexyl rings in **3** and **4** are twisted in the same direction, and to approximately the same extent. The major qualitative difference concerns the forms of the Newman projections given in Figure 4. While the disilane shows a regular, alternating (FB)₃ projection,²⁸ the nearly eclipsed cyclohexyls in the diphosphine have “gone past” one another to give a nonalternating F₂B₂ projection.²⁸ This difference is no doubt a consequence of the strong pyramidal nature of the phosphine moiety, which causes a significant decrease in the C-P-C projection angle. Indeed, symmetric expansion of the C-P-C projection angle to equal the C-Si-C projection angle leads to practically identical Newman projections.³²

Conclusions

The present study has demonstrated a marked similarity in the static stereochemistry of tetraalkyldisilanes and tetraalkyldiphosphines. In each of the two classes of compounds, the gauche isomer is a significant component of the conformational equilibrium mixture, which increases in relative importance with increasing steric bulk of the alkyl group. In the case of the tetra-*tert*-butyl compounds, the gauche form is essentially the exclusively populated isomer. The remarkable similarity in the X-ray structures of tetracyclohexyldisilane (**3**) and tetracyclohexyldiphosphine (**4**) provides strong support for the main thesis of this paper: that conformational preferences in tetraalkyldiphosphines are primarily dictated by the same steric factors as in the corresponding disilanes, and that there is therefore no compelling need to invoke special electronic effects. This conclusion extends into the dynamic domain, since site exchange between the two nonequivalent *tert*-butyl groups in tetra-*tert*-butyldisilane (**2**) and tetra-*tert*-butyldiphosphine, involving enantiomerization of the gauche forms, requires 13.8 and 12.6 kcal/mol, respectively. That special electronic effects play no significant role in the static and dynamic stereochemistry of diphosphines (excluding, of course, processes involving pyramidal inversion at phosphorus³³) is quite consistent with the rapid decrease in the magnitude of the “gauche

effect" with increasing separation of the bonded atoms bearing the lone pairs,³⁴ an effect which also finds expression in the less than 1 kcal/mol preference of diphosphine itself for the gauche form.³

In summary, with regard to rotation about the central bond, the conformational behavior of tetraalkyldiphosphines closely parallels that of the analogous disilanes. Since EFF calculations have proven highly successful in the conformational analysis of polysilanes, as demonstrated in this and previous^{15b} work, we conclude that the EFF method may be successfully extended to the conformational analysis of polyphosphines.^{35,36}

Experimental Section

DNMR Measurements. ¹H NMR spectra were recorded at 100 MHz on a Varian XL-100 spectrometer operating in the Fourier transform mode. The spectrometer was locked on ²H present in the solvent, deuteriochloroform. Temperatures, considered to be accurate to ± 2 °C, were measured with a copper-constantan thermocouple.

1,1,2,2-Tetra-tert-butylidisilane (2). This compound, prepared as previously described,³⁷ had mp 31.5–33 °C (lit.³⁷ mp 32–33 °C); NMR spectrum (-42.5 °C) δ_{CDCl_3} (Me₄Si) 1.09 (9 H, s, *t*-Bu), 1.14 (9 H, s, *t*-Bu), and 3.67 (1 H, s, Si-H).

1,1,2,2-Tetracyclohexyldisilane (3). A procedure analogous to the synthesis of **2** was used in the preparation of **3**. Potassium metal (0.85 g, 0.022 mol) was melted in refluxing cyclohexane (50 mL) under a dry nitrogen atmosphere. Dicyclohexylchlorosilane³⁸ (5.00 g, 0.022 mol) was added dropwise, and the resulting black mixture was refluxed for 2 h. After filtration under dry nitrogen, removal of the solvent under reduced pressure gave a white solid. Recrystallization from *n*-pentane yielded a crystalline solid (0.92 g, 21.7%). mp 99.0–100.0 °C. The ¹H NMR spectrum featured resonances at δ_{CDCl_3} (Me₄Si) 0.80–2.05 (22 H, m, cyclohexyl H) and 3.45 (1 H, br s, Si-H).

Anal. Calcd for C₂₄H₄₆Si₂: C, 73.76; H, 11.86; Si, 14.37. Found: C, 73.47; H, 11.87; Si, 14.28.

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Supplementary Material Available: Final positional and thermal parameters, standard deviations, and two additional stereoviews of **3** (4 pages). Ordering information is given on any current masthead page.

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- By equating the free rotation dipole moment (μ_{fr} , eq i)²¹ and the dipole moment for a mixture (μ , eq ii), eq iii is obtained.

$$\mu_{\text{fr}}^2 = m_1^2 + m_2^2 + 2m_1m_2 \cos \theta_1 \cos \theta_2 \quad (\text{i})$$

$$\mu^2 = \sum_i n_i \mu_i^2 \quad (\text{ii})$$

$$\sum_i n_i \mu_i^2 = m_1^2 + m_2^2 + 2m_1m_2 \cos \theta_1 \cos \theta_2 \quad (\text{iii})$$
 Substitution of eq iv²¹ into eq iii and simplification yields eq v

$$\mu_i^2 = m_1^2 + m_2^2 + 2m_1m_2 (\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi_i) \quad (\text{iv})$$

$$m_1m_2 \sin \theta_1 \sin \theta_2 \sum_i n_i \cos \phi_i = 0 \quad (\text{v})$$

where m_1 and m_2 are the resultant moments at each end of the central bond, θ_1 and θ_2 are the angles m_1 and m_2 make with the bond axis, ϕ_i is the dihedral angle between m_1 and m_2 , and n_i is the mole fraction of conformer i . Equation v is valid if and only if the collection of conformers represented by n_i and ϕ_i will yield the same dipole moment as the free rotation model. If m and θ do not equal zero, a simpler condition is obtained:

$$\sum_i n_i \cos \phi_i = 0 \quad (\text{vi})$$

This condition is met by any statistical mixture consisting of all possible staggered and/or eclipsed conformers obtained by full rotation (2π) of two n -fold ($n > 1$) rotors around a central bond, assuming standard geometries. This includes the 2:1 mixture of gauche and anti conformers of R₂HM-MHR₂.

- O. Exner, "Dipole Moments in Organic Chemistry", Georg Thieme Verlag, Stuttgart, 1975.
- Free rotation (or "windmilling") is an illusory concept in principle, i.e., on grounds of symmetry. For a relevant discussion, see J. Reisse, R. Ottinger, P. Bickart, and K. Mislow, *J. Am. Chem. Soc.*, **100**, 911 (1978).
- The torsional angle ϕ was held fixed at a given value (ϕ_0) by imposing a large quadratic potential $E_{\text{rx}} = 10\,000(\phi - \phi_0)^2$ kcal/mol. This technique is a modified version of one originally employed by K. B. Wiberg and R. H. Boyd, *J. Am. Chem. Soc.*, **94**, 8426 (1972).
- H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).
- The torsional profile was calculated by starting at a minimum and rotating one end of the molecule in small increments of 5–10°. At each point a specific dihedral angle was frozen,²³ and all other geometrical parameters were completely relaxed.
- As expected,²⁸ nonalternating, F₂BFB₂ structures occur along the torsional circuit of **2**.
- As shown in Figure 1, our calculation of the torsional profile of **2** uncovered several additional local minima.
- W. D. Hounshell, D. A. Dougherty, and K. Mislow, *J. Am. Chem. Soc.*, **100**, 3149 (1978).
- A priori, one would expect $3^4 = 81$ forms for both gauche and anti **3**, since each structure is represented by four descriptors, and each descriptor can take on three different values. For the gauche conformation (considering only one enantiomer) there are nine C₂ forms, leaving 72 asymmetric structures. However, since each asymmetric structure is represented twice (equivalent structures may be thought of as interconvertible by rotation around an axis analogous to the C₂ axis of the symmetric structures), there are only 9 + 36 = 45 gauche forms. Similarly, there are 60 asymmetric and 21 symmetric anti structures. The latter consist of three forms with C_{2v} symmetry and six each with C_i, C_s, and C₂ symmetry. However, since each structure with C_i, C_s, and C₂ symmetry is represented twice (if one does not distinguish enantiomers of the C₂ forms), the symmetric structures are therefore reduced to 12 unique forms. Furthermore, each C₁ form is represented four times in the 60 asymmetric structures (again considering enantiomers to be indistinguishable). The total number of unique anti structures is therefore reduced to 12 + 15 = 27.
- In the present context, the term "global minimum" refers to the structure of lowest energy among those found on the potential energy hypersurface. Although only a complete mapping of the hypersurface would permit un-

ambiguous identification of the true global minimum, practical considerations rule out such an approach in systems as complex as those studied here.

- (31) See, for example, J. F. Blount and K. Mislow, *Tetrahedron Lett.*, 909 (1975); D. A. Dougherty, K. Mislow, J. F. Blount, J. B. Wooten, and J. Jacobus, *J. Am. Chem. Soc.*, **99**, 6149 (1977); D. A. Dougherty, F. M. Llori, J. F. Blount, and K. Mislow, *Tetrahedron*, **34**, 1301 (1978).
- (32) The structure of tetracyclohexylethane, though gauche like **3**, is quite dissimilar in other respects (S. G. Baxter, unpublished results; Professor C. Rüchardt, personal communication).
- (33) The inversion barrier at phosphorus in 1,2-diphenyl-1,2-dimethyldiphosphine is ca. 26 kcal/mol (J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *J. Am. Chem. Soc.*, **90**, 6401 (1968)). Thus pyramidal inversion is very slow on the time scale of P-P bond rotation.
- (34) S. Wolfe, L. M. Tel, J. H. Liang, and I. G. Csizmadia, *J. Am. Chem. Soc.*, **94**, 1361 (1972).
- (35) The conformational analysis of polyphosphines, including the cyclopolyphosphines, has recently attracted attention; see, for example, A. L. Rheingold, Ed., "Homoatomic Rings, Chains and Macromolecules of Main-Group Elements", American Elsevier, New York, N.Y., 1977.
- (36) Work on the static and dynamic stereochemistry of tetraaryldisilanes is in progress, and will be reported in due course.
- (37) K. Triplett and M. D. Curtis, *J. Organomet. Chem.*, **107**, 23 (1976).
- (38) F. Metras and J. Valade, *Bull. Soc. Chim. Fr.*, 1423 (1965).

Substituent Effects in the Phenylbicyclo[2.2.2]octane Ring System by ^{19}F and ^{13}C NMR. The Nature of Aryl ^{19}F NMR Polar Field Effects¹

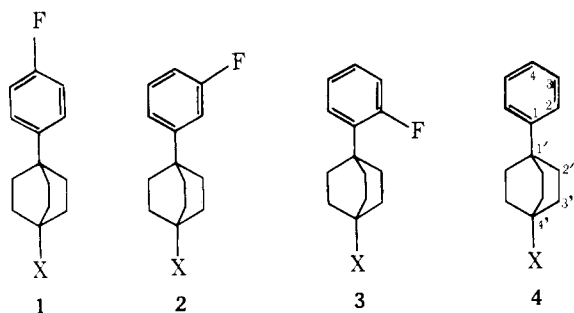
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Abstract: A number of bridgehead-substituted phenylbicyclo[2.2.2]octyl and (*o*-, *m*-, and *p*-) fluorophenylbicyclo[2.2.2]octyl derivatives have been synthesized and their ^{13}C and ^{19}F NMR spectra have been recorded. The substituent chemical shifts (SCS) of these stereochemically well-defined model systems permit, for the first time, a quantitative assessment of aryl NMR polar field effects in the complete absence of other electronic mechanisms. The results clearly establish field-induced π polarization (F_π) as an important mechanism of transmission of polar substituent effects. The relative magnitude of this effect at the meta and para positions of monosubstituted benzene derivatives is quantitatively defined. The dual nature of ^{19}F NMR polar field effects is confirmed and the two components (direct field (F_D) and field-induced π polarization (F_π)) determining this phenomenon are dissected. This enables the coefficient (A) of the Buckingham equation for linear electric field effects on $\text{C}_{\text{sp}^2}\text{-F}$ bonds to be calculated as well as the proportionality constant relating F_π determined ^{19}F and ^{13}C SCS. Unequivocal experimental evidence for reversed ^{19}F NMR polar field effects is also presented. Significant polar solvent shifts in the model systems are discussed.

Introduction

Although the difference of opinion^{2,3} concerning the nature of aryl ^{19}F NMR polar field effects has now been largely reconciled,^{4,5} the quantitative evaluation of the relative magnitude of the components (direct field (F_D) and field-induced π polarization (F_π) effects)⁶ determining this phenomenon is still a subject for deliberation. In order to shed further light on this question we decided to study the ^{19}F NMR spectra of three new model systems (1-X-4-(*p*-, *m*-, and *o*-fluorophenyl)bicyclo[2.2.2]octanes (**1**, **2**, and **3**, respectively)) in conjunction



with a ^{13}C NMR study of 1-X-4-phenylbicyclo[2.2.2]octanes (**4**).

The phenylbicyclo[2.2.2]octyl skeletal framework seemed eminently suited for this purpose for several reasons: (1) the skeletal framework allows the construction of stereochemically well-defined model systems in which the orientation (angle/distance factors) of the substituent relative to the probe center(s) is fixed; (2) the substituent (X) is effectively insulated

from the phenyl ring; thus a definitive experimental estimate of the effects of remote polar groups on aryl chemical shifts (^{19}F and ^{13}C) may be obtained in the complete absence of localized π -electron interactions (mesomeric and inductomesomeric effects); (3) the large number of bonds intervening between the probe (^{19}F or ^{13}C) and the substituent (X) ensures that σ induction is inoperative⁷; (4) substituent-induced structural changes and steric effects should be avoided; (5) no critical and tenuous assumptions regarding the relative sensitivity of sp^2 - and sp^3 -carbon-bound fluorine nuclei to electronic influences need be made when the data are compared with those from fully conjugated aryl fluorides;⁸ (6) an estimate of the relative magnitude of field-induced π polarization effects (F_π)^{4,5} at carbon centers C-4 and C-3 in system 4 by ^{13}C NMR, together with an estimate of the relative magnitude of ^{19}F NMR polar field effects ($F_D + F_\pi$) in systems **1** and **2**, may provide a reasonably quantitative disentanglement of direct field effects (F_D) in these systems. Hence A in the Buckingham equation ($\text{SCS} = AE_z$ where E_z is the direct field component along the CF bond)⁹ for linear electric field effects may then be unambiguously evaluated; (7) a consideration of orientational factors suggests that reversed ^{19}F NMR polar field effects should be observed in system **3**, a phenomenon previously sought after in other model aryl fluorides but to no avail;^{7b} (8) since the substituent dipole is aligned along the major axis of the ring system, the definition of the relative magnitude of F_π effects at C-4 and C-3 in system 4 should bear directly on similar polarization influences at the para and meta carbon positions of monosubstituted benzene derivatives.¹⁰ This is important since, although the latter system has been