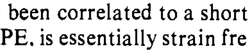
Structure of Hexaphenylethane and Congeners as Determined by Empirical Force Field Calculations

W. Douglas Hounshell, Dennis A. Dougherty, John P. Hummel, and Kurt Mislow*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received July 22, 1976*

Abstract: The structure of hexaphenylethane (HPE) has been computed using full relaxation empirical force field calculations. Three minima on the potential hypersurface are found, corresponding to structures with D_3, S_6, and D_{3d} symmetry. The D_3 ground state is calculated to be more stable than the latter conformers by 2.55 and ca. 44 kcal/mol, respectively. The D_3 ground-state structure, composed of two homochiral trityl propellers, is virtually eclipsed, whereas the S_6 form, composed of heterochiral propellers, is perfectly staggered. Both conformers suffer from severe front strain between the component trityl moieties, as evidenced by major deformations of C-C-C bond angles and by the lengthened central C-C bond r_c (1.64 Å). The calculated value of r_c is likely to be a lower limit due to neglect of anharmonic and possible electronic effects. In this context, r_c has been calculated for a variety of polyarylethanes related to HPE. Stabilization of these structures by cross and back clamping has been correlated to a shortened r_c. A study of HPE homologues has revealed that hexaphenyldisilane, in marked contrast to HPE, is essentially strain free, as are the higher members in the homologous series Ph_3MMPh_3. A simple force field model for this series has been devised which is capable of rationalizing changes in strain energy and conformation as a function of M-M bond distance.

Hexaphenylethane (HPE) has been a focal point of chemical interest since Gomberg's initial investigation of "triphenylmethyl" in 1900.[1] In 1968, it was proven that the dimer of triphenylmethyl (trityl) radicals, generally assumed to be HPE, actually has the now well-known methylenecyclohexadiene structure (**1**).[2] A fascinating historical account of "The Hexaphenylethane Riddle" has been provided by McBride.[3]



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Although HPE remains to be synthesized, there has been considerable work in recent years on the general class of compounds Ph_3MMPh_3 (M = group IVa element), notably in conjunction with bond dissociation,[4] infrared and Raman (stretching force constant) studies,[5] and x-ray structure determinations,[6] and on several "clamped" hexaarylethanes[7-12] (see below). Our own interest in this field arose directly from previous investigations in this laboratory dealing with molecular propellers in which a complement of aryl rings is attached to a central methane[13,14] or ethane[15] hub. The present paper describes the application of empirical force field calculations to the ground-state structures of HPE and several of its congeners. In several cases we calculate highly strained molecules, whose structural features lie outside the range for which the force field was directly parametrized. However, given the previous successful calculations of the related, but less strained, triaryl[16,17] and tetraaryl[14,15] systems, it is anticipated that the trends and general structural features which result from these calculations are nevertheless reliable.

Hexaphenylethane (HPE)

Symmetry Considerations. The highest symmetries possible for HPE are D_{3d} and D_{3h} (the symmetries of a staggered and an eclipsed ethane skeleton, respectively). With the superposition of six twofold rotors (i.e., the phenyl rings) onto the ethane skeleton, and with rotation about the central ethane bond, the point group symmetry can be reduced to any subgroup of D_{3d} or D_{3h}. All of these conformations of HPE may be described by a central dihedral angle, ϕ_c (C_{phenyl}-C_{ethane}-C_{ethane}-C_{phenyl}), which refers to torsion about the central bond, and by the individual phenyl ring dihedral angles, ϕ_r (C_{ethane}-C_{ethane}-C_{phenyl}-C_{ortho}), which refer to the orientations of the various phenyl rings. By convention, the sign of the dihedral angle (A-B-C-D) is defined as positive if, looking down the B-C bond axis from B to C, a counterclockwise rotation of the B-C-D plane is required to eclipse the A-B and C-D bonds; the dihedral angle is 0° for the eclipsed conformation. Two distinct conformations of HPE with D_{3d} symmetry are possible, designated as *closed* (${}^cD_{3d}$: $\phi_r = 0°$; $\phi_c = 60°$) and *open* (${}^oD_{3d}$: $\phi_r = 90°$; $\phi_c = 60°$) to describe the appearance of the faces of the phenyl rings when the molecule is viewed down the central ethane bond axis.[18]

On the basis of our previous work,[13-17] it seems reasonable to expect that the ground-state conformation of HPE is one in which both trityl moieties are helical when viewed along the threefold axis.[19] There are two distinct types of molecular propeller conformations: an achiral (meso) form, with point group symmetry S_6, in which the two trityl moieties are heterochiral, i.e., have opposite helicities ($\phi_c = 60°$; all $|\phi_r|$'s equal, with the ϕ_r's of the two ends having opposite signs), and a chiral (racemic) form, with point group symmetry D_3, in which the two trityl moieties are homochiral, i.e., have the same helicity (no restriction on ϕ_c; all ϕ_r's equal in magnitude and sign).

Calculated Ground State. A full relaxation empirical force field approach was used to calculate the strain energies and geometries of several conformations of HPE. The force field and program have been previously described.[16] The input structures were optimized using the pattern search minimization technique with an energy criterion for minimization of 0.01 kcal/mol over one iteration. The structures were optimized *without symmetry constraints.*

Four input structures were considered, all with $\phi_c = 60°$, corresponding to HPE with ${}^cD_{3d}$, ${}^oD_{3d}$, D_3 ($\phi_r = 45°$), and S_6 ($|\phi_r| = 45°$) symmetries. Each input structure had regular hexagonal phenyl rings, tetrahedral central carbon bond angles, a central bond length (r_c) of 1.56 Å, and a C_{ethane}-C_{phenyl} bond length (r_r) of 1.55 Å. The ${}^cD_{3d}$, D_3, and S_6 input structures relaxed to energy minima without desymmetrization. The ${}^oD_{3d}$ input structure relaxed to a structure with S_6 symmetry. Since torsional potentials are usually shallow, the torsional angles $|\phi_r|$ and ϕ_c of the S_6 and D_3 minima were independently modified in each direction and the structure was then reoptimized. This precaution should generally be taken with nonquadratic energy minimization procedures such as pattern search.[21] The central bond distance (r_c) was similarly modified. The strain energy was not diminished significantly by these

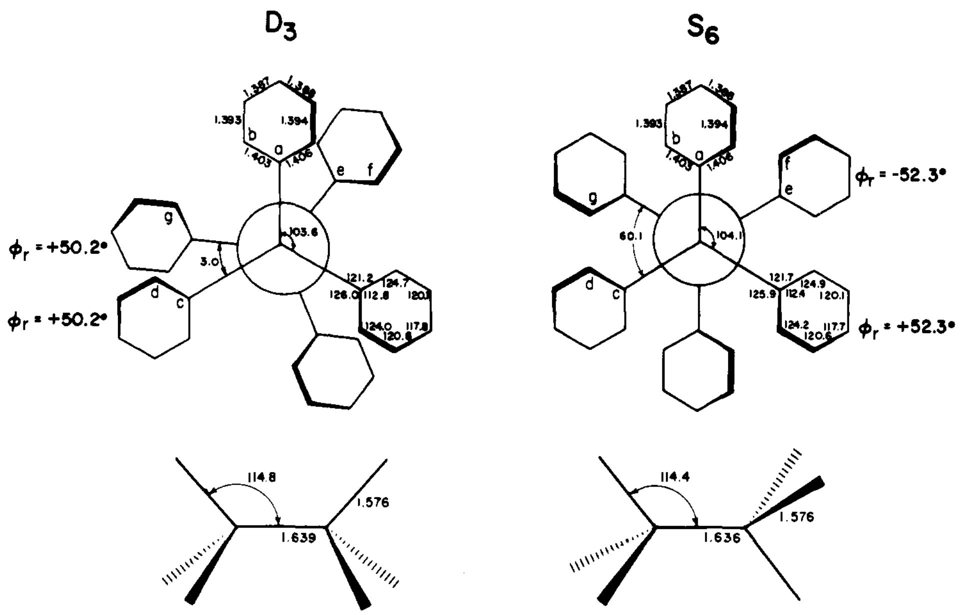


Figure 1. Calculated structural parameters for D_3 and S_6 conformations of HPE.

Table I. Closest[a] Intramolecular Contacts in HPE

	Interaction[b]	D_3		S_6	
		d_{ij}, Å	No. sym eq int[c]	d_{ij}, Å	No. sym eq int[c]
Inter-end	C_a-C_e	2.963	3	3.273	6
	C_a-C_f	2.928	6	3.101	6
	C_b-C_f	2.937	3	3.411	6
	C_a-H_f	2.694	6	2.559	6
	C_b-H_f	(3.102)	6	2.587	6
	H_b-H_g	2.222	3	(3.016)	6
Intra-end	C_a-C_d	2.803	6	2.812	6
	C_b-C_d	3.161	6	3.118	6
	C_b-C_c	3.169	6	3.161	6
	C_a-H_d	2.500	6	2.510	6
	C_b-H_d	2.723	6	2.673	6

[a] C–C less than 3.45 Å (the distance parameter for this interaction,[16] $d_{ij}^* = 3.9$ Å); C–H less than 3.0 Å ($d_{ij}^* = 3.45$ Å);[16] H–H less than 2.7 Å ($d_{ij}^* = 3.0$ Å).[16] [b] This column lists the atoms involved in nonbonded interactions. The subscripts indicate the positions of the atoms (cf. Figure 1). [c] Number of symmetry equivalent interactions.

transformations and structure modifications were minor.

Of the three observed minima on the conformational hypersurface, the one corresponding to the D_3 isomer is lowest in energy. However, the S_6 isomer lies only 2.55 kcal/mol above this ground state.[22,24] The ${}^cD_{3d}$ minimum, which represents an idealized six-ring flip[13] intermediate, is about 44 kcal/mol less stable.[26] Hence, the D_3 (racemic) and S_6 (meso) conformers, i.e., the two propeller forms of HPE, are the only ones which are expected to be significantly populated.

The ground state (D_3) of HPE is nearly eclipsed ($\phi_c = 3.0°$), with the rings ($\phi_r = 50.2°$) on opposite ends of the ethane lying essentially face-to-face; this effect results from the optimal nesting of the two homochiral trityl moieties. On the other hand, the S_6 conformation is perfectly staggered, with the edge of each ring ($|\phi_r| = 52.3°$) directed toward the face of a ring on the opposite end. It is interesting to note that as early as 1958, Adrian[27] had postulated, solely on the basis of inspection of molecular models, that HPE assumes an eclipsed D_3 geometry; the S_6 geometry was apparently not considered. Using a "crude", semiempirical method for calculating the strain energies of structures with fixed geometries, and considering only those nonbonded H-H and C-H interactions which appeared to be severe by inspection of the model, Adrian calculated a ϕ_r of about 40°. Most recently, the intermolecular π complex formed by association of two tris(p-biphenyl)methyl radicals was also assigned eclipsed D_3 symmetry.[28]

Figure 1 summarizes the calculated geometric parameters for the D_3 and S_6 conformers of HPE. It is immediately apparent that certain of these parameters deviate markedly from the standard values. Most strikingly, r_c (1.64 Å) considerably exceeds the normal value of 1.53 Å; r_r (1.58 Å) is also stretched, though to a lesser extent. Furthermore, the three phenyl rings in each moiety are compressed toward each other, closing the $C_{phenyl}-C_{ethane}-C_{phenyl}$ valence bond angle to 104°, and expanding the $C_{ethane}-C_{ethane}-C_{phenyl}$ bond angle to 114°, while the rings themselves are significantly deformed at their centers of attachment to the ethane carbon atom. The conclusion is unavoidable that repulsion between the two trityl moieties (*front strain*) is principally responsible for all major deformations. A more detailed analysis is provided by the information collected in Table I, which lists the closest intramolecular contacts in D_3 and S_6 HPE. It is seen that differences between the d_{ij}'s of the two conformers are greatest for "inter-end" interactions between the two component trityl fragments, but are negligible for "intra-end" interactions within each moiety. In other words, the energy difference between D_3 and S_6 HPE arises principally from the differences in the modes of packing homochiral (D_3) and heterochiral (S_6) trityl propellers, since interactions within each individual propeller are virtually the same for the two forms (as evidenced also by the similarity in geometric parameters). Table I further reveals that the D_3 form suffers most from short C-C and H-H distances, whereas in the S_6 form it is the C-H interactions which are the most severe. Whether in the D_3 or S_6 conformation, HPE is seen to be a severely strained molecule, a point to which we shall return below.

Central Bond Length. The extraordinary value of 1.64 Å calculated for the central bond length of HPE calls for further comment.[29] A survey of the literature indicates that in a number of instances, the length of a bond joining two tetracoordinate carbon atoms is found to equal or exceed 1.6 Å;[30] evidently, a bond length of this order of magnitude is far from unprecedented. Nevertheless, it should be noted that all compounds in our collection[30] with bond lengths greater than that of tri-*tert*-butylmethane (1.611 Å)[30t] are bridged, in the sense that cleavage of one long bond would not allow the

Table II. Comparison of Experimental and Calculated Bond Lengths

Compound	Bond length, Å Exptl (Method)	 Calcd
1,1′-Biadamantane	1.578 (2)[a] (XR)	1.575[b]
Hexamethylethane	1.573 (4)[c] 1.582 (10)[d] (ED)	1.565
Tri-*tert*-butylmethane	1.611 (5)[e] (ED)	1.587[b]

[a] R. A. Alden, J. Kraut, and T. G. Traylor, *J. Am. Chem. Soc.*, **90**, 74 (1968). [b] Reference 31. [c] L. S. Bartell, *Trans. Am. Crystallogr. Assoc.*, **2**, 134 (1966). [d] L. S. Bartell and T. L. Boates, *J. Mol. Struct.*, **32**, 379 (1976). [e] Reference 30t.

molecule to fall apart. Thus, the molecules survive despite the presence of what is most likely a severely weakened bond. HPE does not enjoy such bridging.

Among molecules with abnormally long bonds, some comparisons have been made of experimentally determined bond lengths with those calculated using the empirical force field (Table II). In the case of 1,1′-biadamantane and of hexamethylethane, the agreement between experimental and calculated values for the central bond is satisfactory. However, in the case of tri-*tert*-butylmethane, the Bu-C bond length determined by electron diffraction exceeds the calculated value by ca. 0.02 Å. This discrepancy almost certainly reflects a deficiency in the potential function describing bond stretching. In the present force field,[16,31] this function is harmonic (quadratic), but for an extreme bond length deformation, such as the one suffered by HPE or tri-*tert*-butylmethane, an anharmonicity term should be added.[32] Although the inclusion of such a term would give a value for r_c in HPE somewhat in excess of the estimated 1.64 Å, we have chosen not to quantify this effect due to the paucity of experimentally determined long bonds in molecules amenable to force field calculations.[33]

On the other hand, the abnormal bond lengthening in lepidopterene[30e] and related compounds,[30a-d,f] recently shown[34] to be primarily the result of through-bond coupling of π systems, is not expected to be significant in HPE (see below).

Other Polyarylethanes

The extraordinary degree of deformation in the molecular framework of HPE, particularly with reference to the central bond, suggests that this molecule labors under an appreciable internal strain and is therefore likely to cleave into trityl radicals with extreme ease. In order to obtain information on the extent to which other polyarylethanes also exhibit central bond stretching, and in the hope of correlating r_c with stability, additional calculations were performed which are summarized in Table III. The structures in this Table were calculated as described above, with two modifications, as follows.

In our previous experience with empirical force field calculations we had found that bond lengths are essentially invariant to the optimization procedure involving variation of torsional angles followed by reminimization; bond angles and dihedral angles also generally change only slightly. Therefore, since our main concern was with variations in r_c, and in order to reduce the cost of the computations, this additional minimization procedure was not performed (with the exception of pentaphenylethane (**8**), see below).

Second, the parameters listed in Table IV were introduced since compounds **2, 3, 4, 5, 10,** and **11** contain biphenyl sub-

Table III. Central Bond Length, Synthesis, and Stability of Polyarylethanes

Compound	Calcd central bond length, r_c, Å	Method of synthesis	Stability	Ref
9,9′-Bisfluorenyl (**2**)	1.543[a]	Radical dimerization	Homolysis near 300 °C	*b*
1,1,2,2-Tetraphenylethane (**TPE**)	1.556[c]	Radical dimerization	No homolysis near 200 °C	*d*
Tris(biphenylene)ethane (**3**)[e]	1.560	Cationic rearrangement	Mp 473–475 °C	*f*
9,9′-Biphenylidene-(9,9′)-bisfluorenyl (**4**)[e]	1.565	Intramolecular radical combination	Mp 385 °C	*f*
Bisfluoradenyl (**5**)[e]	1.565[g]	Radical dimerization	Mp 306–307 °C	*h*
1,1,2,2-Tetrakis(2,6-xylyl) ethane (**6**)	1.574[i]	Radical dimerization (with Cr^{2+})	Irreversible homolysis at 220 °C	*j*
Bitriptycyl (**7**)[e]	1.586	Bianthryl + benzyne	Mp 577 °C (dec, in absence of O_2)	*k*
Pentaphenylethane (**8**)	1.595[l]	Radical combination	$\tau_{1/2}$ (80°) = 42.5 min;[m] mp 160 °C dec	*n*
2,2,3,3-Tetraphenylbutane (**9**)	1.597[o]	Radical dimerization	$\tau_{1/2}$ (60°) = 54 min;[m] mp 124 °C	*p,q*
9,9′-Diphenyl-(9,9′)-bis-fluorenyl (**10**)[e]	1.603[r]	Radical dimerization	Mp 221 °C dec; absorbs O_2 slowly in soln at room temp	*s*
9,9′,10,10′-Tetraphenyl-9,10-dihydrophenanthrene (**11**)[e]	1.615	Intramolecular radical combination	Mp 340 °C (no dec); unreactive to O_2 in soln reacts with K in soln	*t*
1,1,1,2,2-Pentaphenyl-propane (**12**)	1.627	Unknown[u]		
Hexaphenylethane (HPE)	1.639 (D_3) 1.636 (S_6)	Unknown		

[a] This value refers to the gauche ground state. For the anti form r_c = 1.551 Å. [b] I. C. Lewis and T. Edstrom, *J. Org. Chem.*, **28**, 2050 (1963); I. C. Lewis and L. S. Singer, *Carbon*, **5**, 373 (1967). [c] Reference 15. This value refers to the anti ground state. For the gauche form r_c = 1.575 Å. [d] J. Coops, W. Th. Nauta, M. J. E. Ernsting, and A. C. Faber, *Recl. Trav. Chim. Pays-Bas*, **59**, 1109 (1940). [e] See Figure 2. [f] Reference 7. [g] This value represents the gauche ground state. For the anti form r_c = 1.565 Å. [h] Reference 12a. [i] Reference 15. [j] Reference 2. [k] Reference 9. [l] This value refers to the nonhelical ground state. For the helical form r_c = 1.601 Å. [m] Reaction with O_2 in the presence of a hydrogen donor. [n] W. E. Bachmann and F. Y. Wiselogle, *J. Org. Chem.*, **1**, 354 (1936). [o] This value refers to the anti ground state. For the gauche form r_c = 1.613 Å. [p] S. C. W. Hook, *Tetrahedron Lett.*, 3321 (1975). [q] S. C. W. Hook and B. Saville, *J. Chem. Soc., Perkin Trans. 2*, 589 (1975). [r] This value refers to the gauche ground state. For the anti form r_c = 1.612 Å. [s] W. Schlenk, A. Herzenstein, and T. Weickel, *Chem. Ber.*, **43**, 1753 (1910); ref 8. [t] Reference 10. [u] Preliminary results suggest that **12** does not form from the corresponding radicals (D. A. Dougherty, unpublished results).

Table IV. Force Field Parameters for Biphenyl[a]

	Stretch			
	k_r			r°
$C_{bi}-C_{bi}$	5.35			1.46
	Bend ($k_3' = -0.401$)			
	k_θ			θ°
$C_{ar}-C_{bi}-C_{bi}$	0.35			120°
	Twist			
	V_0	B	n	ϕ_{max}
$C_{ar}-C_{bi}-C_{bi}-C_{ar}$	−2.80	−1	2	90°

[a] Potential functions and parameter units are given in ref 16. C_{bi} = carbon atom involved in biphenyl bond. C_{ar} = aryl carbon.

structures for which the force field[16,31] had not been previously parametrized.[35]

Included in the series of polyarylethanes are several known compounds which are formally hexaarylethanes.[39] We have found it useful to classify these structures into two general types (cf. Figure 2). In the first, which we describe as *back clamped*, aryl rings attached to the *same* ethane carbon atom are connected to each other by a chain of one or more bonds (intra-end bonding). In the second type, a chain of one or more bonds joins aryl rings which are attached to *different* ethane carbon atoms (inter-end bonding). Such structures are termed *cross clamped*.

Conformations. Prior to discussing trends in r_c values (Table III), a description of the salient conformational features of the polyarylethanes is in order (cf. Table V).

The calculated D_3 structure of tris(biphenylene)ethane (**3**) is in agreement with that assigned by Wittig and Schoch[7] on the basis of ^{1}H NMR data. The D_{3h} form, for which we calculate a relative steric energy of ca. 110 kcal/mol, resembles a double three-ring flip transition state[13] (cf. Figure 2) for the interconversion of the D_3 enantiomers. It is therefore predictable that **3** will be optically stable under ordinary conditions.

2,2,3,3-Tetraphenylbutane (**9**) minimized in both gauche and anti C_2 conformations; the anti isomer was calculated to be 5.1 kcal/mol more stable than the gauche. Similar results had previously been obtained for 1,1,2,2-tetraphenylethane (TPE).[15] By contrast, the gauche conformer (C_2) of 9,9′-diphenyl-(9,9′)-bisfluorenyl (**10**) and of 9,9′-bisfluorenyl (**2**) was calculated to be 10.5 and 6.6 kcal/mol more stable, respectively, than the corresponding anti structure (C_{2h}); further, bisfluoradenyl (**5**) is more stable in the gauche form by 1.5 kcal/mol. Thus, each compound which contains a fluorenyl moiety is predicted to have a gauche ground state. It is interesting to note in this connection that 10,10′-dianthronyl, which is structurally similar to **2**, has been shown to be gauche in the crystalline state[30q] and in solution[40].

Compound **11**, a singly cross clamped derivative of HPE, resembles the latter in having virtual D_3 symmetry, in the sense that all ϕ_r's are equally signed. Similarly, the calculated structure of 1,1,1,2,2-pentaphenylpropane (**12**), a heretofore unreported compound, is interesting in its overall similarity to that of D_3 HPE, in which a sixth phenyl ring replaces the methyl group of **12**.

Surprisingly, in light of the quasi-D_3 structure of **12**, pentaphenylethane (**8**) minimized to a nonhelical[19] ground state. Accordingly, all ϕ_r's and ϕ_c in **8** were modified, followed by reminimization. The resulting structures were still essentially the same as the original nonhelical structure. Further exploration of the energy surface did, however, reveal a helical minimum, with a strain energy of 6.5 kcal/mol relative to that of the nonhelical ground state.

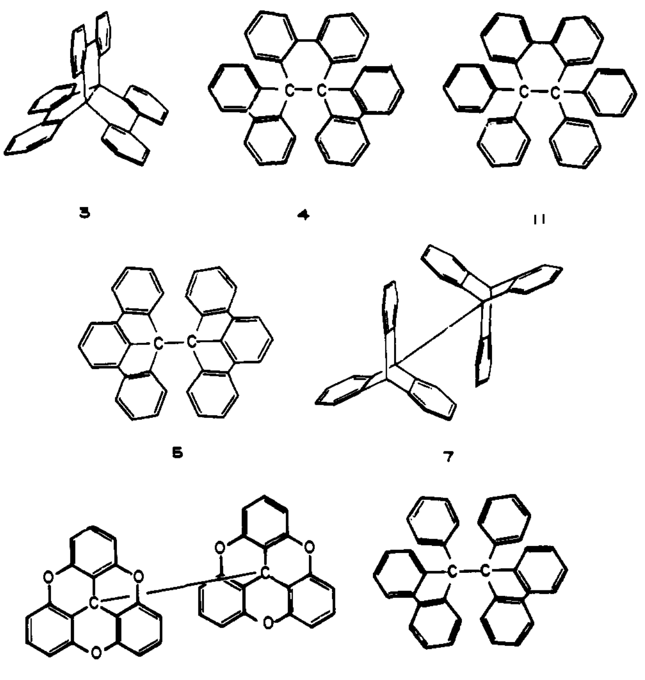


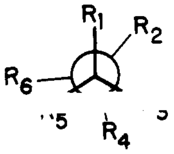
Figure 2. Examples of clamped hexaarylethanes. Structures **5**, **7**, **10**, and **13** are back clamped; **3** and **11** are cross clamped; **4** is both back and cross clamped. All formulas shown are intended to convey only molecular constitutions; conformational ground states are not implied in the perspective renditions (**3**, **7**, **13**).

Electronic Effects. The electronic effect[34] previously described in reference to the bond lengthening observed in lepidopterene[30e] and related compounds[30a-d,f] might conceivably affect the structures of certain back clamped molecules which contain a fluorenyl moiety. Substructures of this type restrict ϕ_r to values around 60-75°, close to the optimum value (90°) for through-bond coupling of the aromatic π orbitals. For example, the experimental[30q] central σ bond length of 1.60 Å in 10,10′-dianthronyl is significantly longer than would be expected on the basis of the calculated value for **2** (1.543 Å). Thus, the experimental values of r_c for **2**, **4**, **5**, and **10** are expected to be somewhat larger than those calculated by the force field method.

It is anticipated that the effect will be smaller in unclamped molecules. In an unclamped system, the π orbitals of the rings are no longer forced into a position of favorable overlap with the σ bond, although, in principle, overlap may be substantial at the equilibrium position. However, the effect is apparently not operative in TPE, for which the calculated r_c value of 1.556 Å compares favorably with the x-ray value[41] of 1.555 Å for 1,1,2,2-tetrakis(2-methoxyphenyl)ethane. Thus, steric considerations alone serve to account for the bond length in TPE, and we presume the same for HPE.

Stability. The stability of polyarylethanes correlates well with r_c, the value of which is determined by three interrelated factors: internal strain, clamping effects, and electronic effects; the stability of the radical products of homolysis is expected to play a subsidiary role.[42] The expected correlation between r_c and the tendency toward homolysis is apparent from inspection of Table III. The series TPE, **6**, **8**, **9**, and **12** clearly shows that unclamped polyphenylethanes with longer calculated central bond lengths undergo homolysis with greater ease. The fact that pentaphenylpropane (**12**) has an r_c value which is intermediate between that of the known phenanthrane (**11**) and HPE makes it an interesting synthetic objective. In all of these considerations it should be kept in mind that an anharmonicity correction would somewhat increase the r_c's listed in Table III, especially for values of $r_c \geqslant 1.6$ Å. However, the *trend* in r_c values, and therefore the force of the arguments presented in this paper, would remain unaffected.

Table V. Calculated Conformations of Polyarylethanes[a]



Compd	Pt Gp	Sym equiv R's	ϕ_r[b]	ϕ_c[c]
2[d]	C_2	$R_1 + R_3 =$	64.3, −62.2, 64.0, −61.5	44.6, −69.6,
		$R_2 + R_6 =$		55.3, −65.8,
		fluorenyl		55.1, −69.6
		$R_4 = R_5 = H$		
TPE[e]	C_2	$R_1 = R_4 = H$		61.8, −53.2,
		$R_2 = R_3 = Ph$	−74.8, −72.6	61.4, −70.1,
		$R_5 = R_6 = Ph$	29.9, 29.7	43.1, −70.4
3	D_3	$R_1 + R_2 =$	−39.0, −39.3, −39.1	59.1, −61.0,
		$R_3 + R_4 =$	−39.3, −39.1, −39.1	59.2, −60.8
		$R_5 + R_6 =$		59.2, −60.8
		biphenylene		
4	C_2	$R_1 + R_6 =$ bi-	28.1, 28.8	74.5, −53.8,
		phenylene	−65.7, 65.1, −65.6, 65.1	57.5, −53.9,
		$R_2 + R_4 =$		74.4, −45.9
		$R_5 + R_3 =$		
		fluorenyl		
5[f]	C_2	$R_1 + R_3 + R_5$	80.8, 89.4, −81.7	54.6, −49.2,
		$= R_6 + R_4 +$	80.2, 89.4, −81.0	55.2, −48.9,
		$R_2 =$ fluor-		55.1, −97.0
		adenyl		
7	D_{3d}	$R_l + R_3 + R_5$	−1.3, 1.0, 0.5	59.8, −59.8,
		$= R_2 + R_4 +$	0.7, −1.5, 0.8	60.2, −60.0
		$R_6 =$ trip-		60.1, −60.2
		tycyl		
8[g]	C_1	$R_1 = Ph$	39.3	30.0, −99.6,
		$R_2 = Ph$	25.4	41.0, −77.4,
		$R_3 = Ph$	92.0	35.5, −76.5
		$R_4 = Ph$	86.2	
		$R_5 = Ph$	−20.2	
		$R_6 = H$		
9[h]	C_2	$R_1 = R_4 = Me$		51.4, −67.5,
		$R_2 = R_3 = Ph$	86.8, 87.9	51.2, −69.9,
		$R_5 = R_6 = Ph$	6.3, 6.1	50.6, −69.5
10[i]	C_2	$R_1 = R_2 = Ph$	−2.3, −3.7	58.8, −72.8,
		$R_3 + R_5 = R_6$	78.1, −73.7, 79.3, −74.2	48.9, −57.9,
		$+ R_4 =$		48.6, −73.0
		fluorenyl		
11	C_2	$R_1 + R_2 =$ bi-	−48.9, −49.3	70.9, −39.9,
		phenylene		
		$R_3 = R_6 = Ph$	−34.7, −34.2	81.7, −46.4,
		$R_4 = R_5 = Ph$	−13.4, −14.6	81.4, −39.7
12	C_1	$R_1 = Ph$	63.1	9.7, −109.4,
		$R_2 = Ph$	68.4	17.4, −105.2,
		$R_3 = Ph$	31.1	8.3, −110.1
		$R_4 = Ph$	32.5	
		$R_5 = Ph$	54.3	
		$R_6 = Me$		

[a] All input structures had $\phi_C = 60°$. The input values of ϕ_r were: 45° (helical) for **8**, anti and gauche 9, **11**, and **12**; 90° for anti 5 (the input for gauche **5** was a rotated anti minimum); 0° for 4, 7, and gauche **10**; ±60° (fluorenyl) for anti and gauche **2**; and ±60° (fluorenyl), 0° (Ph) for anti **10**. [b] Listed in the same order as the R's in the adjacent column. [c] Listed in the order: R_1–R_2, R_2–R_3, R_3–R_4, R_4–R_5, R_5–R_6, R_6–R_1. [d] Gauche ground state; anti minimum is 6.6 kcal/mol higher in energy. [e] Reference 15. Anti ground state; gauche minimum is 4.9 kcal/mol higher in energy. [f] Gauche ground state; anti minimum is 1.5 kcal/mol higher in energy. [g] Nonhelical ground state; helical minimum is 6.5 kcal/mol higher in energy. [h] Anti ground state; gauche minimum is 5.1 kcal/mol higher in energy. [i] Gauche ground state; anti minimum is 10.5 kcal/mol higher in energy.

The stabilizing effect of clamping is also evident from Table III. Back and cross clamping both bring about a diminution in back strain, which is the result of nonbonded interactions between phenyl rings attached to the same ethane carbon, and front strain, which involves phenyl rings attached to different ethane carbons. Back clamping pins rings back, away from the region over the central bond, thereby reducing front strain; at the same time bonds replace what were previously close intra-end nonbonding interactions, resulting in less back strain. In a similar manner a new bond formed in cross clamping reduces front strain while at the same time the movement of the clamped rings toward the central region reduces back strain.

Diphenylbisfluorenyl (**10**) differs from HPE only in that two phenyl rings are back clamped at each end of the molecule. Apparently as a direct result of back clamping, **10** acquires a shorter central bond length and a greater stability. Although **8**, **9**, and **10** have essentially the same calculated r_c (Table III), the lesser stability of **10** relative to the unclamped molecules **8** and **9** could at least in part be the result of a further bond lengthening in **10** due to the previously discussed electronic effect. Both **8** and **9** can be handled in the air at elevated temperatures (e.g., recrystallization from benzene), whereas solutions of **10** must be handled in an inert atmosphere. Bitriptycyl (**7**) and bisfluoradenyl (**5**) are more completely back clamped and exhibit even shorter central bonds as well as extremely high thermal stability. It has recently been noted that the stability of **5** is "a question of substantial significance".[12b] As shown in the present calculations, a relatively short central bond results from back clamping and leads to increased stability. In the case of **7**, homolysis is additionally rendered unfavorable by the relative instability of triptycyl radicals, as compared with trityl radicals.[43] However, stabilization of the component radicals does not significantly destabilize a hexaarylethane, as is illustrated by the dimer (**13**) of the sesquixanthydryl radical,[11] a maximally back clamped hexaarylethane.[44] The radical has been shown[11b] to be essentially planar and is therefore expected to be highly resonance stabilized. Nevertheless, the dimer is a relatively stable molecule (mp > 300 °C dec), dissociating to the extent of only 1-2% at 140°.[11b]

Cross clamping has an even greater stabilizing effect than back clamping, for in addition to affording relief of internal strain, as described above, the presence of a cross clamp prevents dissociation of the two triarylmethyl moieties, even if it does not prevent homolysis. Thus, although the singly cross clamped compound, **11**, possesses a fairly extended ethane bond, it is a remarkably stable molecule. The triply cross clamped tris(biphenylene)ethane (**3**) shows an extremely short central bond (for a hexaarylethane) and high thermal stability; its lack of reactivity is abetted by the fact that homolysis gives rise to two radical centers which are sterically inaccessible to other reagents (barring inversion at the ethane carbons).

One of the compounds studied, 9,9′-biphenylidene-(9,9′)-bisfluorenyl (**4**), is both back clamped and cross clamped. This triply clamped hexaarylethane has essentially the same calculated central bond length as tris(biphenylene)ethane (**3**), which is triply cross clamped. The calculated bond length of **4** is much shorter than that of **11**, in which the back clamps are absent, and **10**, in which the cross clamp is absent.

In summary, the stability of hexaarylethanes is enhanced by cross and/or back clamping, and, for a given structural type, the tendency toward homolysis is a function of r_c and, to a lesser extent, of homolysis product stability. Considering these factors, HPE is seen to be the least stable of all the molecules considered in this study, and its preparation therefore presents a major challenge to the synthetic organic chemist.

Stereochemically Correspondent Molecules

A number of x-ray structures have been determined of molecules which are stereochemically correspondent[13,20,45] to HPE, in the sense that there are six twofold rotors (i.e., Ph- or Me_2N-[46]) symmetrically attached to two atoms which form

Table VI. X-Ray Structures of Molecules Which Are Stereochemically Correspondent to Hexaphenylethane[a]

Molecule	Sym[b]	r_c', Å	r_r', Å	ϕ_c', deg	$\lvert\phi_r'\rvert$,[c] deg	Ref
Ph_6Sn_2	S_6	2.780	2.167	60[c]	23, 45, 13	*d*
	S_6	2.759	2.193	60[c]	53, 72, 47	
Ph_6Pb_2	S_6	2.848	2.210	60[c]	23, 47, 10	*e*
	S_6	2.839	2.233	60[c]	51, 72, 50	
$[Ph_3PNPPh_3]^+$	S_6	3.078	1.788	60		*f*
$Ph_3SiNCNSiPh_3$	S_6	5.696	1.838	60	59	*g*
	S_6	5.698	1.878	60	38	
	D_3	5.744	1.833	56[c]	54, 50	

[a] Parameters r_c', r_r', ϕ_c', and ϕ_r' are defined in analogy to r_c, r_r, ϕ_c, and ϕ_r for HPE (cf. text); in the bottom two entries, the PNP and SiNCNSi units are linear arrays corresponding to the ethane central bonds. [b] For Ph_6Sn_2 and Ph_6Pb_2, the symmetry of the two crystallographically independent molecules in each case is strictly C_i (three different ϕ_r''s on each heterochiral propeller). For "D_3"—$Ph_3SiNCNSiPh_3$, the symmetry is strictly C_3 (two different ϕ_r''s, one for each of the two homochiral propellers). The slight deviations from S_6 and D_3 symmetry are ascribed to crystal packing forces. [c] Calculated from the reported crystal coordinates. [d] Reference 6a. [e] Reference 6b. [f] R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, **96**, 7601 (1974). [g] Reference 48.

Table VII. Si-Si Force Field Parameters for Hexaphenyldisilane[a]

	Stretch			
	k_r			r°
Si-Si[b]	1.85			2.345
	Bend ($k_3' = -0.401$)			
	k_θ			θ°
C_{ar}-Si-Si[c]	0.32			109.0
	Twist			
	V_0	B	n	ϕ_{max}
C_{ar}-C_{ar}-Si-Si[d]	0.014	1	6	30°
C_{ar}-Si-Si-C_{ar}[e]	0.40	1	3	60°

[a] Potential functions and parameter units are given in ref 16. [b] Reference 51. [c] Estimated value based on C_{sp3}-Si-Si bend.[51] [d] Estimated value based on C_{ar}-Si-C_{ar}-C_{ar} torsion.[14] [e] Estimated value based on C_{sp3}-Si-Si-C_{sp3} torsion.[51]

Table VIII. Comparison of Geometric Parameters Calculated for Hexaphenylethane and -disilane[a]

		HPE	HPDS	Ψ-HPDS
D_3	r_c	1.639	2.369	2.357
	r_r	1.576	1.864	1.861
	θ_1	114.8	109.4	108.7
	θ_2	103.6	109.5	110.2
	ϕ_c	3.0	7.2	5.4
	ϕ_r	50.2	48.0	50.1
S_6	r_c	1.636	2.374	2.358
	r_r	1.576	1.866	1.860
	θ_1	114.4	109.7	109.6
	θ_2	104.1	109.3	109.4
	ϕ_c	60.1	59.9	60.0
	ϕ_r	52.3	50.7	51.4
	ΔE_T (S_6-D_3)	2.55	0.92	0.88
${}^cD_{3d}$	r_c	1.634	2.398	2.370
	r_r	1.603	1.882	1.873
	θ_1	111.7	108.8	108.7
	θ_2	107.1	110.1	110.2
	ϕ_c	60.0	60.0	60.0
	ϕ_r	0.0	0.0	0.0
	ΔE_T (${}^cD_{3d}$-D_3)	44.15	8.81	8.78

[a] The parameters r_c, r_r, ϕ_c, and ϕ_r, defined in the text for HPE, and θ_1 and θ_2, defined for HPE as C_{ethane}-C_{ethane}-C_{phenyl} and C_{phenyl}-C_{ethane}-C_{phenyl}, respectively, may be extended to HPDS and Ψ-HPDS by substituting Si for C_{ethane}. ΔE_T = difference in steric energy. Units for r, θ, ϕ, and ΔE_T are Å, deg, deg, and kcal/mol, respectively.

part of a linear array. The essential structural features of the hexaphenyl systems are summarized in Table VI. It is noteworthy that approximate S_6 symmetry is exhibited in each case except for Ph_3Si-N=C=N-$SiPh_3$, in which the unit cell contains two molecules with S_6 and two with D_3 symmetry.[48] In particular, hexaphenyldiplumbane and hexaphenyldistannane, molecules of formula type Ph_3MMPh_3 and therefore formally homologues of HPE, both exhibit virtual S_6 symmetry (cf. Table VI, footnote *b*) in the crystal, whereas the calculated ground state of HPE has D_3 symmetry. It therefore became of interest to determine the molecular structure of the missing links.[49] Attempts to obtain a crystal structure of hexaphenyldisilane (HPDS) and of hexakis(*p*-tolyl)disilane were frustrated by disorder in the crystal.[50] We therefore resorted to empirical force field calculations.

Hexaphenyldisilane. The parameters required for the calculations were in part available from previous work in this laboratory on silanes[14] and on compounds containing Si-Si bonds.[51] Table VII lists additional parameters which were needed in the present work, and which were therefore derived from those employed in the earlier studies. The same four input structures were used as for HPE (${}^cD_{3d}$, ${}^oD_{3d}$, D_3, and S_6), with equilibrium bond lengths (r_c° and r_r°). As in the case of HPE, ${}^cD_{3d}$, D_3, and S_6 relaxed to energy minima without desymmetrization. The ${}^oD_{3d}$ input structure relaxed to a D_3 conformation. The S_6 and D_3 minima were optimized by modifying $\lvert\phi_r\rvert$ and ϕ_c in both directions and then reminimizing the energy of the structure.

The calculated ground state of HPDS has D_3 symmetry, but the S_6 conformation is now only 0.92 kcal/mol higher in energy (as compared with 2.55 kcal/mol for HPE),[24] and the ${}^cD_{3d}$ six-ring flip intermediate of HPDS lies only 8.81 kcal/mol above D_3 (as compared with 44.15 kcal/mol for HPE). The torsional angles are comparable with those in HPE: the D_3 conformation is nearly eclipsed (ϕ_c = 7.2°), with ϕ_r = 48.0°; the $\lvert\phi_r\rvert$ of the S_6 conformation is 50.7°. That HPDS is less strained than HPE is evidenced by the minimal distortion of the phenyl rings and central bond angles in HPDS, and of the central Si-Si bond (r_c = 2.37 Å,[52] as compared with 2.33 and 2.34 Å for disilane[53] and hexamethyldisilane,[54] respectively). The relevant parameters for HPE and HPDS are compared in the first two columns of Table VIII.

A Force Field Model for Ph_3MMPh_3

As was noted above, although the relatively strain-free HPDS still prefers the essentially eclipsed D_3 ground state, and in that sense closely resembles the highly strained and deformed HPE molecule, the difference in steric energy (ΔE_T) between D_3 and S_6 conformers has significantly decreased. Since hexaphenyldistannane and hexaphenyldiplumbane have S_6 symmetry in the crystal,[6] the question naturally arose whether there might be a crossover in calculated ground-state

Table IX. Geometric Parameters Calculated for Structures of Type Ph_3MMPh_3[a]

		D_3					S_6					
$r_c°$	$r_r°$	r_c	ϕ_r	ϕ_c	θ_1	Rel E_T	r_c	ϕ_r	ϕ_c	θ_1	Rel E_T	ΔE_T (S_6–D_3)
1.512[b]	1.500[b]	1.639	50.2	3.0	114.8	78.57	1.636	52.3	60.1	114.4	81.12	2.55
1.95	1.715	1.995	50.6	4.6	111.5	19.02	1.998	53.0	60.1	111.7	20.93	1.91
2.345	1.913	2.353	43.3	12.6	109.9	2.44	2.355	49.8	60.0	110.0	2.79	0.35
2.45	1.965	2.455	30.7	25.3	109.9	1.56						
2.55	2.015	2.551	24.6	32.0	109.6	1.07	2.551	43.9	60.0	109.7	1.32	0.25
(NT)[c]		(2.549)	(36.6)	(18.2)	(109.6)	(0.00)						(1.32)
2.65	2.065	2.647	19.2	38.6	109.4	1.15	2.651	25.0	60.0	109.8	1.35	0.20
2.77	2.125	2.765	15.5	42.3	109.0	1.65	2.767	20.1	60.0	109.5	1.75	0.10
(NT)[c]		(2.765)	(24.5)	(30.2)	(109.4)	(1.18)						(0.57)
3.00	2.24	2.993	4.5	54.9	109.0	3.86	2.994	14.0	60.0	109.3	3.87	0.01

[a] For a definition of parameters and units, see Table VIII, footnote *a* (M is substituted for C_{ethane}). Rel E_T is the steric energy (kcal/mol) relative to the least strained calculated member of this series (arbitrarily given the value $E_T = 0.00$). Note also that a comparison of total steric energy, E_T (eq 1 in ref 16) is strictly valid only for calculations of stereoisomeric structures (cf. footnote 22 in ref 14). [b] Parameters for carbon in existing force field.[16] The entries on this line were obtained for HPE as described in the text. [c] NT = no torsional potential, i.e., the structure in the immediately preceding entry was recalculated taking $V_0 = 0.0$ for ϕ_c.

symmetry (from D_3 to S_6) with an increase in bond lengths (r_c and r_r). To investigate this problem, and at the same time to gain some insight into the way in which bond and dihedral angles change as bond lengths are varied in the series Ph_3MMPh_3, we resorted to a force field approach in which HPE was used to represent the entire class of compounds; this approach was necessitated by the fact that suitable force field parameters have not been developed for M = Ge, Sn, or Pb. Each homologue was considered to be identical with HPE except for the equilibrium M–M and M–C_{aryl} bond lengths ($r_c°$ and $r_r°$, respectively). The hydrocarbon parameters were used for all other potentials. A similar model had been successfully employed before in a study of triarylmethane systems.[55]

By use of this method, structures of Ph_3MMPh_3 can be calculated for any combination of r_c and r_r, not just for combinations which correspond to actual molecules; note that M–M can represent a linear array of more than two atoms (e.g., $Ph_3C–C{\equiv}C–CPh_3$). The assumptions behind this model are that the geometry and ΔE_T are primarily determined by interactions between the phenyl rings of the molecule, the severity of which depends on variations in r_c and r_r, and not on the nature of M. One difficulty with this model is that the height (V_0) of the ϕ_c torsional potential is expected to be lower for longer bonds, but since there is not enough information on torsional barriers about long bonds, we have no reasonable way to calibrate V_0 as a function of $r_c°$. The maximum effect of the reduced torsional potential can be calculated by assuming no barrier ($V_0 = 0.0$). The torsional barrier is not expected to affect S_6 conformations since $\phi_c = 60°$ is already at the minimum of the torsional potential curve; on the other hand, D_3 conformations are expected to be stabilized by relaxation to a more eclipsed conformation as V_0 approaches zero.

A Test of the Model. Having in hand a calculated structure for HPDS, we were in a position to test our model by comparing this structure with one calculated for a "stretched" HPE, constructed by setting the equilibrium bond lengths ($r_c°$ and $r_r°$) equal to those in the silicon force field. All other force constants were retained from the hydrocarbon force field. The D_{3d}, S_6, and D_3 input structures for this fictitious molecule (Ψ-HPDS) were minimized as for HPDS, with further optimization of the S_6 and D_3 minima. The structures of all three Ψ-HPDS conformations and their relative energies were in satisfactory agreement with the geometries and energy differences of HPDS calculated by using the full silicon force field (cf. the last two columns of Table VIII). The satisfactory simulation of HPDS by Ψ-HPDS inspires some confidence in the validity of our approach.

In an extension of this test, a Ψ-Ph_6Sn_2 structure was calculated using the method already described, with $r_c° = 2.77$ Å and $r_r° = 2.18$ Å, the average of the x-ray values.[6a] In marked contrast to HPE and HPDS, in which the D_3 ground state is nearly eclipsed and ϕ_r = ca. 50°, the D_3 conformer of Ψ-Ph_6Sn_2 was found to be nearly staggered ($\phi_c = 46.8°$), with $\phi_r = 11.8°$. The S_6 isomer ($|\phi_r| = 16.7°$ vs. ca. 50° for HPE and HPDS) was found to be only slightly less stable than the D_3 ground state, with $\Delta E_T = 0.11$ kcal/mol. Although the energy difference between D_3 and S_6 is expected to increase slightly with a reduction of the ϕ_c torsional potential, ΔE_T does not exceed ca. 0.6 kcal/mol even when $V_0 = 0.0$. In light of this almost negligible difference, lattice packing forces may easily be held accountable for the observed[6a] S_6 symmetry of hexaphenyldistannane in the crystalline state;[56] alternatively, since ΔE_T is well within the uncertainty of the computational method,[24] the ground state of the free molecule might also have S_6 symmetry.

Interdependence of Steric Energy and of Geometric Parameters. The drastic change in geometry in going from HPDS to Ph_6Sn_2 is in marked contrast to the constancy in geometry in going from HPE to HPDS. This observation led us to calculate a more complete series of Ph_3MMPh_3 structures, using the model described above. Structures were calculated for values of $r_c°$ over the range 1.512 to 3.0 Å. In order to provide a constant basis for the relationship between $r_c°$ and $r_r°$, the covalent radius of the aryl carbon was held fixed at 0.74 Å;[58] thus $r_r° = r_c°/2 + 0.74$. In all calculations, two input structures were used, one with D_3 and the other with S_6 symmetry, both with $\phi_c = 60°$ and $|\phi_r| = 45°$. No reoptimization was performed since this procedure generally proves to be costly and changes the geometry and energy only slightly. Structures with D_3 symmetry for $r_c° = 2.55$ and 2.77 Å were also calculated assuming a zero central torsional potential, in order to determine the maximum effect of reducing the torsional barrier about the lengthened central bond. The salient results of this series of calculations are collected in Table IX.

Inspection of Table IX reveals that the relative steric energy (E_T) remains small (≤4 kcal/mol) for values of $r_c°$ between 2.35 and 3.0 Å, with a minimum at ca. 2.55 Å (presumably due to an optimum in nonbonded attractions), but that for shorter central bond lengths, E_T increases drastically. The central MMC valency angle (θ_1) faithfully reflects this behavior: this angle remains virtually tetrahedral (109.5°) so long as $r_c° \geqslant$ 2.35 Å, but for shorter central bond lengths, θ_1 begins to open up significantly; this has the effect of relieving front strain at the expense of back strain.

Throughout the range of $r_c°$'s, the D_3 conformation is calculated to be slightly more stable than the S_6 form.[24] Here too, the difference is negligible for central bond distances greater than 2.35 Å, but rapidly increases at shorter distances.[59]

In summary, changes in E_T, ΔE_T, and θ_1 become appreciable only at $r_c° \leqslant 2.35$ Å, when front strain begins to become severe.

The relationships of ϕ_c and ϕ_r to r_c (Table IX) are depicted in Figure 3. As the central bond is shortened, ϕ_r for both conformers (D_3 and S_6) opens up from 10° until, at $r_c < 2.35$ Å, the curve levels off to a value slightly greater than 50°. Concurrently, the central dihedral angle of the D_3 conformer closes down from just over 50° at r_c = ca. 3.00 Å until, with $r_c < 2.35$ Å, the curve rapidly levels off to a value just above 0°, i.e., to the eclipsed conformation. In fact, as Figure 3 reveals at a glance, the sigmoid ϕ_c curve for D_3 is virtually the mirror image of the ϕ_r curve, indicating that $\phi_c + \phi_r$ is nearly constant at about 55°. That is, as the central torsional angle closes toward the eclipsed position, the rings flatten away from the area of inter-end contact. The effect of a zero central torsional potential (cf. Table IX) on the D_3 structures is to move both the ϕ_r and ϕ_c curves to the right of Figure 3 (more eclipsed at the same r_c), while retaining the relationship between ϕ_c and ϕ_r.

The relationship $\phi_r + \phi_c \approx 55°$ holds for the entire series of Ph_3MMPh_3 structures with D_3 symmetry. It seems reasonable to suppose that the remarkable constancy of this relation is the result of a compensating effect involving a counterbalancing of two unfavorable nonbonded interactions, C_b-C_f and H_b-H_g (cf. Table I). Further inspection of the closest interactions shows how the structure of HPE is determined by a balance of front and back strain effects.

The small changes in ϕ_c and ϕ_r brought about by increasing r_c in HPE to ca. 2 Å suggest that although r_c in HPE may be longer than the calculated 1.64 Å due to neglect of anharmonicity and electron delocalization effects, no significant conformational changes will result.

An Overview. A coherent picture emerges from these computations which has the virtue of internal consistency, is capable of accommodating all of our numerical results, and accords nicely with chemical intuition. Consider bringing together two Ph_3M moieties from a distance (r_c) of, say, 10 Å. Because r_c and r_r are very large compared with normal bond distances, there is virtually no interaction between the phenyl rings and ϕ_c as well as ϕ_r may assume virtually any value. As r_c decreases and the six rings begin to sense each other's presence, each Ph_3M moiety relaxes into a propeller conformation (local C_3 symmetry), initially with very small angles of twist (ϕ_r). At about this point (ca. 3 Å) the structure enters one of two channels on the potential energy hypersurface, depending on whether the Ph_3M moieties are homo- or heterochiral. From this point on and until r_c = ca. 2.3 Å, the *energy* of the two conformers (E_T) changes only slightly and ΔE_T is negligible. Concurrently, however, marked *conformational* changes accompany the decrease in r_c, both in terms of ϕ_c, as the D_3 form rapidly changes from a virtually staggered conformation to one which is almost eclipsed,[60] and in terms of ϕ_r, as the phenyl rings in both D_3 and S_6 forms twist by ca. 40° in order to accommodate themselves to the ever narrowing distance between the inter-end phenyl rings. Finally, at central bond distances of less than ca. 2.3 Å, all conformational degrees of freedom (with respect to changes in ϕ_r and ϕ_c) have been lost, as the two component propellers are now firmly pressed against each other in both conformers so that a further shortening of r_c can only result in gross molecular deformations (bending of θ_1 and θ_2, stretching of r_c) resulting from front strain. The cutoff point of ca. 2.3 Å coincides with the hexaphenyldisilane system. Hexaphenylethane, with r_c well below the 2.3 Å cutoff, is highly strained and grossly deformed; the above considerations show why it is that HPE occupies a special position among molecules of the type Ph_3MMPh_3 with respect to strain energy and molecular deformation.[61]

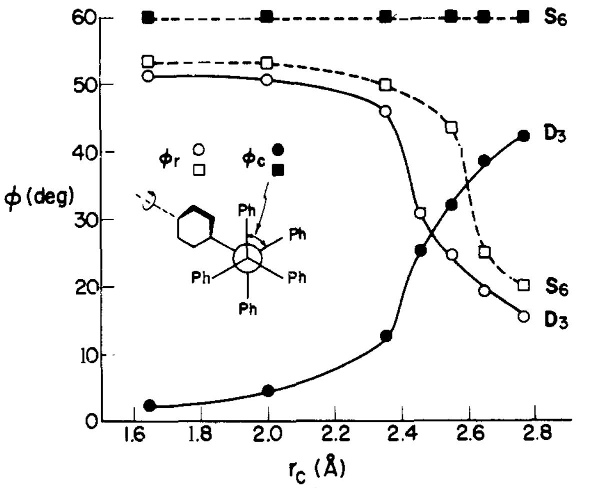


Figure 3. Dihedral angles ϕ_r (open symbols) and ϕ_c (black symbols) of D_3 (circles) and S_6 (squares) conformers of Ph_3MMPh_3 as a function of r_c.

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References and Notes

(1) M. Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900); *Chem. Ber.*, **33**, 3150 (1900).

(2) H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968).

(3) J. M. McBride, *Tetrahedron*, **30**, 2009 (1974).

(4) R. E. Dessy, P. M. Weissman, and R. L. Pohl, *J. Am. Chem. Soc.*, **88**, 5117 (1966).

(5) (a) P. A. Bulliner, C. O. Quicksall, and T. G. Spiro, *Inorg. Chem.*, **10**, 13 (1971); (b) L. A. Harrah, M. T. Ryan, and C. Tamborski, *Spectrochim. Acta*, **18**, 21 (1962).

(6) (a) H. Preut, H.-J. Haupt, and F. Huber, *Z. Anorg. Allg. Chem.*, **396**, 81 (1973); (b) H. Preut and F. Huber, *ibid.*, **419**, 92 (1976).

(7) G. Wittig and W. Schoch, *Justus Liebigs Ann. Chem.*, **749**, 38 (1971).

(8) H. A. Staab, K. S. Rao, and H. Brunner, *Chem. Ber.*, **104**, 2634 (1971).

(9) C. Koukotas, S. P. Mehlman, and L. H. Schwartz, *J. Org. Chem.*, **31**, 1970 (1966).

(10) G. Wittig and H. Petri, *Justus Liebigs Ann. Chem.*, **505**, 17 (1933).

(11) (a) M. J. Sabacky, C. S. Johnson, Jr., R. G. Smith, H. S. Gutowsky, and J. C. Martin, *J. Am. Chem. Soc.*, **89**, 2054 (1967); (b) E. Müller, A. Moosmayer, A. Rieker, and K. Scheffler, *Tetrahedron Lett.*, 3877 (1967).

(12) (a) H. Rapoport and G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 934 (1960); (b) G. Baum and H. Shechter, *J. Org. Chem.*, **41**, 2120 (1976).

(13) K. Mislow, *Acc. Chem. Res.*, **9**, 26 (1976), and references cited therein.

(14) M. G. Hutchings, J. D. Andose, and K. Mislow, *J. Am. Chem. Soc.*, **97**, 4553 (1975).

(15) P. Finocchiaro, D. Gust, W. D. Hounshell, J. P. Hummel, P. Maravigna, and K. Mislow, *J. Am. Chem. Soc.*, **98**, 4945 (1976).

(16) J. D. Andose and K. Mislow, *J. Am. Chem. Soc.*, **96**, 2168 (1974).

(17) J. F. Blount and K. Mislow, *Tetrahedron Lett.*, 909 (1975).

(18) This notation is analogous to the one used for $^{a}D_{2d}$ and $^{c}D_{2d}$ tetraphenylmethane.[14]

(19) It should be remembered that the classification of a moiety as helical (i.e., as a propeller) depends upon one's point of view.[20] In the present work the propeller axis is considered to be the central ethane bond, and thus a di- or triarylmethyl moiety is regarded as helical if all ϕ_r's have the same sign.

(20) K. Mislow, D. Gust, P. Finocchiaro, and R. J. Boettcher, *Fortschr. Chem. Forsch.*, **47**, 1 (1974).

(21) D. N. J. White and O. Ermer, *Chem. Phys. Lett.*, **31**, 111 (1975).

(22) The equilibrium composition of D_3 and S_6 HPE is determined by ΔG. When comparing stereoisomers, steric energy differences can be reasonably equated with ΔH. Since D_3 is chiral, it is favored relative to S_6 by R in 2, due to entropy of mixing.[23] In contradistinction, the entropy contribution due to symmetry[23] favors S_6 by $R \ln 6 - R \ln 3 = R \ln 2$, exactly counterbalancing the entropy of mixing factor. Thus, ΔG can be equated with differences in steric energy between S_6 and D_3 structures.

(23) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, pp 32, 214–215, 280.

(24) It has been pointed out[25] that force field calculations are less reliable in their predictions of relative conformer energies than in their predictions of structural features. For example, it has recently been shown[25b] that the ground state of 1,2-diphenylpropane is experimentally anti, whereas a

gauche conformer is calculated to be more stable. For this reason, the calculated D_3–S_6 energy difference must be regarded with reservation.

(25) (a) J. D. Dunitz and H. B. Bürgi, *MTP Int. Rev. Sci: Org. Chem.* Butterworths, London, 1976, p 81ff. (b) J. Jacobus, *Tetrahedron Lett.*, 2927 (1976).

(26) (a) An estimate of the width of the $^{c}D_{3d}$ minimum was obtained by modifying ϕ_r and allowing relaxation. It was found that changing all ϕ_r's by 7° was followed by relaxation back toward the $^{c}D_{3d}$ minimum, while a change of 8° led to a D_3 structure. Changing $|\phi_r|$ by 25° to an S_6 structure was followed by relaxation back toward $^{c}D_{3d}$, while a change of 30° gave an S_6 structure. (b) Since D_3 and D_{3d} have the same symmetry number, D_3 is additionally favored over $^{c}D_{3d}$ by $R \ln 2$ (0.41 kcal/mol at 300 K) due to entropy of mixing.[23]

(27) F. J. Adrian, *J. Chem. Phys.*, **28**, 608 (1958).

(28) W. Broser, H. Kurreck, and W. Niemeier, *Tetrahedron*, **32**, 1183 (1976).

(29) That HPE might be destabilized by central bond lengthening has long been recognized (K. Ziegler and F. Ditzel, *Justus Liebigs Ann. Chem.*, **473**, 194 (1929).

(30) We do not claim that the following list is exhaustive. The experimental bond lengths (in Å) are given before each reference. Two bond lengths in parentheses are for two molecules in the unit cell. (A) Structures which are benzenoid dimers: (a) 1.610, B. K. Selinger and M. Sterns, *Chem. Commun.*, 978 (1969); (b) 1.61, M. Ehrenberg, *Acta Crystallogr., Sect. B*, **24**, 1123 (1968); (c) 1.61, M. Ehrenberg, *Acta Crystallogr.*, **20**, 177 (1966); (d) 1.616, J. Gaultier, C. Hauw, J. P. Desvergne, and R. Lapouyade, *Cryst. Struct. Commun.*, **4**, 497 (1975); (e) (1.639, 1.645), J. Gaultier, C. Hauw, and H. Bouas-Laurent, *Acta Crystallogr., Sect. B*, **32**, 1220 (1976); (f) 1.77, M. Ehrenberg, *Acta Crystallogr.*, **20**, 183 (1966). (B) Structures in which the long bond is part of a three- or four-membered ring: (g) 1.600, Y. C. Wang and S. H. Bauer, *J. Am. Chem. Soc.*, **94**, 5651 (1972); (h) 1.60, J. Konnert and I. L. Karle, *J. Cryst. Mol. Struct.*, **1**, 107 (1971); (i) 1.60, M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.*, **94**, 773 (1972); (j) 1.617, E. Ōsawa, H. Henke, and G. Schröder, *Tetrahedron Lett.*, 847 (1976); (k) 1.628, G. I. Birnbaum, *Acta Crystallogr., Sect. B*, **28**, 1248 (1972); (l) 1.629, M. J. Cardillo and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 2399 (1970); (m) 1.63, 1.62, G. L. Hardgrove, L. K. Templeton, and D. H. Templeton, *J. Phys. Chem.*, **72**, 668 (1968); (n) 1.643, C. S. Gibbons and J. Trotter, *Can. J. Chem.*, **51**, 87 (1973); (o) 1.66, 1.60, N. Camerman and A. Camerman, *J. Am. Chem. Soc.*, **92**, 2523 (1970); (p) (1.836, 1.780), R. Bianchi, G. Morosi, A. Mugnoli, and M. Simonetta, *Acta Crystallogr., Sect. B*, **29**, 1196 (1973); see also H. B. Bürgi, E. Shefter, and J. D. Dunitz, *Tetrahedron*, **31**, 3089 (1975). (C) Miscellaneous structures: (q) 1.60, M. Ehrenberg, *Acta Crystallogr.*, **22**, 482 (1967); (r) 1.603, K. B. Birnbaum and G. Ferguson, *Acta Crystallogr., Sect. B*, **25**, 720 (1969); (s) 1.61, H. Mizuno, K. Nishiguchi, T. Otsubo, S. Misumi, and N. Morimoto, *Tetrahedron Lett.*, 4981 (1972); (t) 1.611, H. B. Bürgi and L. S. Bartell, *J. Am. Chem. Soc.*, **94**, 5236 (1972); (u) 1.614, K. W. Muir and G. A. Sim, *J. Chem. Soc. B*, 667 (1968); (v) 1.615, O. Dideberg and L. Dupont, *Acta Crystallogr., Sect. B*, **28**, 3014 (1972); (w) 1.615, H. Iwamura, Y. Tanabe, and H. Kobayashi, *Tetrahedron Lett.*, 1987 (1976); (x) 1.62, I. L. Karle and A. V. Fratini, *Acta Crystallogr., Sect. B*, **26**, 596 (1970); (y) 1.627, Y.-L. Oh and E. N. Maslen, *Acta Crystallogr.*, **20**, 852 (1966); (z) 1.64, 1.63, 1.60, N. Kikutani, Y. Iitaka, Y. Kobayashi, I. Kumadaki, A. Ohsawa, and Y. Sekine, *Acta Crystallogr., Sect. B*, **31**, 1478 (1975); (aa) 1.660, 1.646, S. R. Hall and E. N. Maslen, *Acta Crystallogr.*, **18**, 265 (1965); (bb) (1.674, 1.678), (1.615, 1.613), V. N. M. Rao, C. J. Hurt, K. Kusuda, J. C. Calabrese, and R. West, *J. Am. Chem. Soc.*, **97**, 6785 (1975).

(31) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973).

(32) L. S. Bartell and H. B. Bürgi, *J. Am. Chem. Soc.*, **94**, 5239 (1972).

(33) None of the other structures in ref 30 (except for those listed in 30c, e, and f; cf. ref 34) could be calculated since the presence of small rings, heteroatoms, naphthalene systems, or conjugated double bonds in these molecules precludes the use of the present force field, which is not parametrized for these structural units.

(34) D. A. Dougherty, W. D. Hounshell, H. B. Schlegel, R. A. Bell, and K. Mislow, *Tetrahedron Lett.*, 3479 (1976).

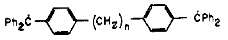
(35) The parameters in Table IV were developed to give a satisfactory correlation between calculated and experimental (ED[36] and XR[37]) structures of biphenyl. Using these parameters, good agreement between the experimental[36] and calculated structures (nonhelical, C_2) of 1,3,5-triphenylbenzene was obtained.

(36) O. Bastiansen, *Acta Chem. Scand.*, **3**, 408 (1949); A. Almennigen and O. Bastiansen, *Skr., K. Nor. Vidensk. Selsk.*, 4 (1958).

(37) J. Trotter, *Acta Crystallogr.*, **14**, 1135 (1961); A. Hargreaves and S. H. Rizvi, *ibid.*, **15**, 365 (1962); G.-P. Charbonneau and Y. Delugeard, *Acta Crystallogr., Sect. B*, **32**, 1420 (1976).

(38) Y. C. Lin and D. E. Williams, *Acta Crystallogr., Sect. B*, **31**, 318 (1975).

(39) Another class of hexaarylethanes (i) has been described by Wittig. (G. Wittig, *Acc. Chem. Res.*, 7, 6 (1974)). Since none of the compounds (i) were



isolated or characterized (molecular weight determinations were carried out on solutions of the diyls generated in situ from the corresponding dichloro compounds by reaction with copper), we have not considered them in the present study.

(40) H. H. Huang, *Aust. J. Chem.*, **29**, 2415 (1976).

(41) J. J. Daly, F. Sanz, R. P. A. Sneeden, and H. H. Zeiss, *J. Chem. Soc., Perkin Trans. 2*, 1614 (1972).

(42) Cf. W. J. leNoble, "Highlights of Organic Chemistry", Marcel Dekker, New York, N.Y., 1974, p 626.

(43) P. D. Bartlett and F. D. Greene, *J. Am. Chem. Soc.*, **76**, 1088 (1954).

(44) Empirical force field calculations could not be performed on **13** since the program[16] is not parametrized for oxygen.

(45) (a) D. Gust, P. Finocchiaro, and K. Mislow, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 3445 (1973); (b) J. G. Nourse, *ibid.*, **72**, 2385 (1975).

(46) $(Me_2N)_6Mo_2$[47a] and $(Me_2N)_6W_2$[47b] have been prepared and exhibit virtual $^{c}D_{3d}$ symmetry in the crystal.

(47) (a) M. Chisholm, F. A. Cotton, B. A. Frenz, and L. Shive, *Chem. Commun.*, 480 (1974); (b) F. A. Cotton, B. R. Stults, J. M. Troup, M. H. Chisholm, and M. Extine, *J. Am. Chem. Soc.*, **97**, 1242 (1975).

(48) G. M. Sheldrick and R. Taylor, *J. Organomet. Chem.*, **101**, 19 (1975).

(49) It has been reported[6a] that hexaphenyldigermane is not isomorphous with hexaphenyldistannane and -diplumbane.

(50) J. F. Blount, personal communication.

(51) J. P. Hummel, J. Stackhouse, and K. Mislow, unpublished work.

(52) The actual value of r_c for HPDS may be slightly larger than that calculated by the force field due to through-bond coupling.[34] Cf. also H. Sakurai, S. Tasaka, and M. Kira, *J. Am. Chem. Soc.*, **94**, 9285 (1972); H. Sakurai and M. Kira, *ibid.*, **97**, 4879 (1975); C. G. Pitt and H. Bock, *J. Chem. Soc., Chem. Commun.*, 28 (1972).

(53) B. Beagley, A. R. Conrad, J. M. Freeman, J. J. Monaghan, B. G. Norton, and G. C. Holywell, *J. Mol. Struct.*, **11**, 371 (1972).

(54) B. Beagley, J. J. Monaghan, and T. G. Hewitt, *J. Mol. Struct.*, **8**, 401 (1971).

(55) M. R. Kates, J. D. Andose, P. Finocchiaro, D. Gust, and K. Mislow, *J. Am. Chem. Soc.*, **97**, 1772 (1975).

(56) For example, tetraphenylmethane is calculated[14] to have D_{2d} symmetry, while in the crystal[57] S_4 symmetry is observed. Similarly, biphenyl is found to be twisted (D_2) in the gas phase (electron diffraction)[36] but planar (D_{2h}) in the crystal.[37]

(57) A. Robbins, G. A. Jeffrey, J. P. Chesick, J. Donohue, F. A. Cotton, B. A. Frenz, and C. A. Murillo, *Acta Crystallogr., Sect. B*, **31**, 2395 (1975).

(58) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Interscience, New York, N.Y., 1972, p 117.

(59) The ΔE_T of 0.35 kcal/mol for $r_c° = 2.345$ Å is considerably less than the values calculated for HPDS (0.92 kcal/mol) and Ψ-HPDS (0.88 kcal/mol). The reason is that although $r_c°$ is the same for all three structures, $r_r°$ for the Ph_3MMPh_3 species (1.913 Å, Table IX) is longer than the value for the other two (1.850 Å, see text above); consequently, there is less inter-end repulsion and a smaller differential strain.

(60) For the S_6 isomer, by definition ϕ_c remains invariant at 60°.

(61) HPE also occupies a special position with respect to stereoisomerization mechanisms. Given the great internal strain and long (therefore weak) central C–C bond, and given the relatively high energy of the $^{c}D_{3d}$ form (a possible stereoisomerization intermediate), we believe that conformational interconversions ((R)-$D_3 \rightleftarrows S_6$, (R)-$D_3 \rightleftarrows (S)$-D_3, etc.) in this molecule will almost certainly take place by way of fragmentation to trityl radicals,[62] rather than merely by torsion of phenyl rings. On the other hand, recalling that the $^{c}D_{3d}$ form of HPDS lies only 8.81 kcal/mol above D_3, we believe that hexaphenyldisilane, -digermane, -distannane, and -diplumbane are capable of stereoisomerization by ring flipping. We note in this connection our failure to resolve methyl signals in hexakis(*o*-tolyl)disilane.[63]

(62) However even assuming internal return (i.e., radical dimerization within a solvent cage), these stereomutation pathways may be vitiated by the relatively facile dimerization of trityl radicals to give **1**.[2] Stereomutation is thus an unlikely process for HPE.

(63) E. W. Turnblom, R. J. Boettcher, and K. Mislow, *J. Am. Chem. Soc.*, **97**, 1766 (1975); J. P. Hummel, unpublished work.