

most cases be CH bond cleavage followed by reattachment. It is the case that migration saddle-point structures exist in which the migrating hydrogen remains tightly bound, however the energies of these structures are predicted to be significantly above the barriers to CH bond cleavage.

The electronic structure at these migration saddle points is analogous to that found in hydrogen-abstraction reactions. Furthermore the cause of the high barriers can be traced to a geometric constraint placed on the electronic wave function which forces two triplet coupled orbitals to be proximate.

The Central Bond Length in Hexaphenylethane and Hexakis(2,6-di-*tert*-butyl-4-biphenyl)ethane

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Abstract: In corroboration of previous work,⁴ full relaxation calculations on the D_3 and S_6 conformers of hexaphenylethane (**1**) by several empirical force field (EFF) schemes (MMI, MMPI, MM2), as well as by the MNDO SCF MO method, show that the D_3 form is 2–5 kcal mol⁻¹ more stable than the S_6 conformer, and that the central C–C bond length has a value of 1.60–1.64 (EFF) or 1.68 (MNDO) Å. EFF calculations (MMPI, MM2) on hexakis(2,6-di-*tert*-butyl-4-biphenyl)ethane (**2**) show that the bonding parameters in the hexaphenylethane portion of this structure differ in no significant way from the corresponding parameters in **1**. We thus conclude that either the central bond length of 1.47 (2) Å reported⁸ in a recent X-ray study of **2** is grossly in error, or a novel shrinkage effect is operative in **2**, and by implication in **1**, which is not taken account of in the parametrization of any of the above computational schemes. The chemical implications of the discrepancy between the observed and calculated central C–C bond length are sufficiently important to call for a confirmation of the X-ray structure. The D_3 conformer of **2** is calculated to be more stable than the S_6 form by 4–6 kcal mol⁻¹; given the enormous size of this molecule (C₁₂₂H₁₅₀), such a conformational energy difference is quite small, and the observation⁸ of molecular S_6 symmetry can be readily ascribed to a crystal packing effect.

Hexaphenylethane (**1**), a molecule of historic importance² and a focal point of chemical interest since Gomberg's initial investigation of "triphenylmethyl" at the turn of the century,³ has thus far resisted all attempts at synthesis. We recently reported⁴ a computational study of this elusive molecule, using full relaxation empirical force field (EFF) calculations.⁵ A search of the potential energy hypersurface too low-lying minima, one corresponding to a D_3 structure composed of two essentially eclipsed homochiral trityl propellers, and the other to a S_6 structure composed of two staggered heterochiral propellers. The D_3 form was computed to be the more stable by 2.55 kcal mol⁻¹, a conclusion which was qualitatively confirmed by a hybrid EFF–EHMO calculation.⁶ That both forms were under substantial internal strain was manifest from the marked deviations of some of the calculated structural parameters from standard values. Most strikingly, the central C–C bond lengths calculated for the D_3 and S_6 forms, 1.639 and 1.636 Å, were abnormally long compared to the standard value of 1.53 Å,⁷ evidently as the result of a severe nonbonded repulsion

between the two trityl moieties (*front strain*).

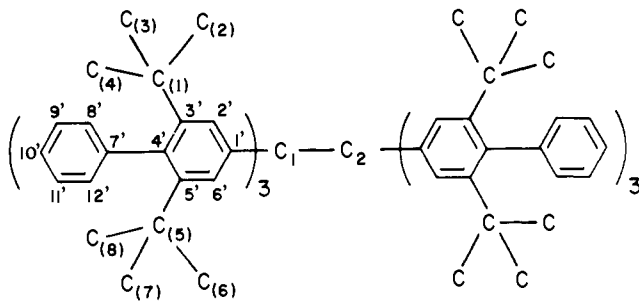
Against this background, the subsequent announcement⁸ by Stein, Winter, and Rieker of the synthesis and X-ray structure of the first, and so far only, unbridged hexaarylethane, hexakis(2,6-di-*tert*-butyl-4-biphenyl)ethane (**2**), was an event of singular import,⁹ not least because much emphasis was placed on the allegation that our predictions⁴ were badly off the mark. First, the finding of an S_6 conformation for **2** was considered contradictory to our prediction of D_3 symmetry for the ground state of **1**; second, **2**, was reported to have the surprisingly short central C–C bond length of 1.47 (2) Å and a C_{ethane}–C_{phenyl} bond length (average value) of 1.65 (3) Å, in marked contrast to the values of 1.636 and 1.576 Å calculated⁴ for S_6 -**1**. The authors suggested⁸ that the presence of the *tert*-butyl groups in **2** might be responsible for these large discrepancies between their findings and our predictions.

(7) A survey of the literature up to 1977⁴ indicates that there are quite a number of instances in which the length of a bond joining two tetracoordinate carbon atoms equals or exceeds 1.6 Å. Some recent, noteworthy additions to this list follow: 1.783, 1.851 Å: Bianchi, R.; Pilati, T.; Simonetta, M. *Acta Crystallogr., Sect. B* 1978, B34, 2157. 1.66 Å: Knox, J. R.; Raston, C. L.; White, A. H. *Aust. J. Chem.* 1979, 32, 553. 1.667 Å: Hisatome, M.; Kawaziri, Y.; Yamakawa, K.; Iitaka, Y. *Tetrahedron Lett.* 1979, 1777. 1.638 Å: Littke, W.; Drück, U. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 406. 1.628 Å: 1.644, 1.616 Å: Ferguson, J.; Mau, A. W.-H.; Whimp, P. O. *J. Am. Chem. Soc.* 1979, 101, 2363, 2370. 1.624 Å: Choi, C. S.; Marinkas, P. L. *Acta Crystallogr., Sect. B* 1980, B36, 2491. 1.671 Å: Polishchuk, V. R.; Antipin, M. Yu.; Bakhmutov, V. I.; Bubnov, N. N.; Solodovnikov, S. P.; Timofeeva, T. V.; Struchkov, Yu. T.; Tumanskii, B. L.; Knunyants, I. L. *Dokl. Acad. Nauk USSR* 1979, 249, 1125. *Dokl. Chem. (Engl. Transl.)* 1979, 249, 547.

(8) Stein, M.; Winter, W.; Rieker, A. *Angew. Chem.* 1978, 90, 737; *Angew. Chem., Int. Ed. Engl.* 1978, 17, 692.

(9) For an account in the popular press, see: *New Sci.* 1978, 80, 606.

(1) (a) Hokkaido University. (b) Princeton University.
 (2) (a) Sholle, V. D.; Rozantsev, E. G. *Russ. Chem. Rev. (Engl. Transl.)* 1973, 42, 1011. (b) McBride, J. M. *Tetrahedron*, 1974, 30, 2009.
 (3) Gomberg, M. *J. Am. Chem. Soc.* 1900, 22, 757; *Ber. Dtsch. Chem. Ges.* 1900, 33, 3150.
 (4) Hounshell, W. D.; Dougherty, D. A.; Hummel, J. P.; Mislow, K. *J. Am. Chem. Soc.* 1977, 99, 1916.
 (5) For recent reviews of the EFF method, see: (a) Dunitz, J. D.; Bürgi, H. B. *MTP Int. Rev. Sci.; Org. Chem., Ser. One* 1976, 81. (b) Ermer, O. *Struct. Bonding (Berlin)* 1976, 27, 161. (c) Allinger, N. L. *Adv. Phys. Org. Chem.* 1976, 13, 1. (d) Altona, C.; Faber, D. H. *Fortschr. Chem. Forsch.* 1974, 45, 1. (e) Osawa, E.; Musso, H. *Top. Stereochem.* in press.
 (6) Dougherty, D. A.; Mislow, K. *J. Am. Chem. Soc.* 1979, 101, 1401.



2

While the disparity between found⁸ S_6 and calculated⁴ D_3 conformations might perhaps be ascribed to the effect of lattice packing forces,¹⁰ the calculation⁴ of an abnormally long C-C bond in the face of precisely the opposite finding^{8,11} presented us with the dismaying prospect of a major failure of the EFF method in the prediction of a structure of central importance in chemistry. Furthermore, by implication, the EFF method might prove to be of dubious value in other cases involving highly strained molecules. Since structures calculated by the EFF method are generally considered to be quite reliable, and have never been so drastically contradicted by experimental observations,⁵ it became essential to address these discrepancies if confidence in the EFF approach as a predictive structural tool was to be retained.¹³

We present here the results of a thorough investigation, along computational lines, of this new "hexaphenylethane riddle".^{2b} The principal questions to be addressed concern the reliability of the previous EFF calculations⁴ on **1**, and the possibility that special substituent effects in **2** might account for the reported⁸ discrepancies.

Results and Discussion

Hexaphenylethane (1). Our previous EFF⁴ and EFF-EHT⁶ calculations had been carried out with the AM force field.¹⁶ In the present work, additional EFF calculations were performed, using Allinger's MMI,^{17,18} MMPI,^{18,19} and MM2²⁰ force fields. Selected structural parameters and energy differences $\Delta\Delta H_f$ ($= (\Delta H_f \text{ of } D_3 \text{ form}) - (\Delta H_f \text{ of } S_6 \text{ form})$) thus obtained are summarized in Table I, together with our previous results.^{4,6} As in the AM force field, the phenyl groups are treated "mechanically" in both MMI and MM2 force fields by assigning special stretch constants to aromatic carbon atoms.²¹ Due to severe congestion

at their points of attachment to the central ethane carbons, the phenyl rings are slightly deformed and take on a "twist-boat" conformation (Table II).²² This slight ring deformation is also evident from the non-uniform endocyclic C-C bond lengths and especially from C-C-C valence angles.⁴ MMPI calculations, which take into account the effect of nonplanarity on resonance energy,^{18,19} gave essentially the same results (Tables I and II). Therefore, the previous "mechanical" treatment of phenyl rings with such small deformations appears to be generally valid.

Calculations with these different force fields uniformly lead to the same conclusion: the D_3 conformer is 2-4 kcal mol⁻¹ more stable than the S_6 conformer, and the repulsion between the two trityl moieties is responsible for all the deformations. The slightly larger deflection of the phenyl rings in the S_6 conformer compared to those in the D_3 conformer reflects the higher overall strain in the former. The central bond length consistently exceeds 1.6 Å with any of the force fields examined. Our original results⁴ are thus shown to be force-field independent.

The results of the EFF calculations were subjected to an additional test by performing full-relaxation MNDO calculations²³ on the two conformers of **1**.²⁴ The final internal coordinates from the MM2 calculations were used as input. In order to save computer time, symmetry constraints were fully imposed and hydrogen atoms were not optimized. The positions of all the carbon atoms were, however, fully optimized by the Davidon-Fletcher-Powell algorithm with the following record:

	D_3	S_6
SCF cycles	55	40
FDP cycles	19	14
CPU time on Hitac M-200H	2 ^h 39 ^m 28 ^s	2 ^h 17 ^s

Structural details as well as the relative energy resulting from these calculations are in good agreement with the EFF results (Tables I and II), except for the central C-C bond lengths (1.68 Å for both conformers), which are significantly longer than the EFF values. In view of the satisfactory performance of the MNDO method in reproducing long bond lengths,^{15,25} it is quite likely that the central bond in **1** is even longer than the values predicted by the various EFF calculations. While the reason for such remarkable bond lengthening in changing from the EFF to the MNDO method is as yet unclear, the difference between MO and EFF results has on occasion been attributed to some special electronic effects that have not been included in the EFF scheme.^{26,27}

Hexakis(2,6-di-*tert*-butyl-4-biphenyl)ethane (2). Even if it is granted that our calculations on **1** are correct, it may still be argued that the *tert*-butyl groups in **2** are responsible for some special effect which leads to an extraordinary contraction of the central C-C bond and a significant expansion of the C_{ethane}-C_{phenyl} bond, thus accounting for the discrepancies under discussion. This possibility was in fact envisaged by Rieker and co-workers.⁸ Since such an effect, assuming its existence, is most likely of steric origin, we decided to perform EFF calculations on **2** itself. For this purpose, we chose two EFF's, namely MMPI and MM2. The

(10) See ref 5a for a discussion of such cases. A classic example is biphenyl, whose ground state is nonplanar, but which adopts a planar conformation in the solid state which is 1.2 kcal mol⁻¹ higher in energy: Almlöf, *J. Chem. Phys.* **1974**, *6*, 135. See also: Charbonneau, G.-P.; Delugeard, Y. *Acta Crystallogr., Sect. B.* **1977**, *B33*, 1586 and references therein. Barrett, R. M.; Steele, D. J. *Mol. Struct.* **1972**, *11*, 105 and references therein.

(11) Considering that the length under dispute refers to a bond between two tetracoordinate carbons in an overcrowded environment, a value of 1.47 Å seems implausible and a priori suspect. Doubts concerning the reliability of this value are reinforced by the authors' caveat⁸ that the bond lengths cited in their paper should be "regarded as preliminary values" ($R = 0.13$) because of the "poor quality of the crystals". However, despite these admitted limitations on the accuracy of their data, the authors remain adamant in their insistence on the essential correctness of their claim.¹²

(12) Professor A. Rieker and Dr. W. Winter, private communications. Winter, W. *Fresenius Z. Anal. Chem.* **1980**, *304*, 279.

(13) A minor discrepancy between the X-ray¹⁴ and the EFF⁴ structures of pentaphenylethane was recently reconciled by the use of a modified force field.¹⁵ See also: Favini, G.; Simonetta, M.; Todeschini, R. *J. Am. Chem. Soc.* **1981**, *103*, 3679 and references therein.

(14) Destro, R.; Pilati, T.; Simonetta, M. *J. Am. Chem. Soc.* **1978**, *100*, 6507.

(15) Osawa, E., manuscript in preparation.

(16) (a) Andose, J. D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 2168. (b) Andose, J. D. et al. *QCPE*, **1978**, *10*, 348.

(17) Wertz, D. H.; Allinger, N. L. *Tetrahedron*, **1974**, *30*, 1579. See also ref 5c.

(18) Allinger, N. L.; Yuh, Y. H. *QCPE*, **1978**, *10*, 318.

(19) (a) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893.

(b) Kao, J.; Allinger, N. L. *Ibid.* **1977**, *99*, 975.

(20) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Allinger, N. L.; Yuh, Y. H. *QCPE* **1981**, *13*.

(21) Aryl carbon atoms are given a lower stretch force constant (8.0667 mdyne/Å) and a shorter natural bond length (1.3937 Å) than the "normal" sp² carbon according to ref 18.

(22) When a benzene ring is bent, a boat form is favored over a chair: Iwamura, H.; Kihara, H.; Misumi, S.; Sakata, Y.; Umemoto, T. *Tetrahedron Lett.* **1976**, 615. However, the energy difference between boat and chair benzene is extremely small for small deformations.

(23) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907. (b) Dewar, M. J. S.; Ford, G. P. *Ibid.* **1979**, *101*, 5558. (c) Thiel, W. *QCPE* **1978**, *11*, 353 as amended by J. McKelvey.

(24) In order to handle such a large molecule, the QCPE program had to be expanded. A copy of the enlarged version of the program may be obtained by writing to one of us (E.O.).

(25) Harano, K.; Ban, T.; Yasuda, M.; Osawa, E.; Kanematsu, K. *J. Am. Chem. Soc.* **1981**, *103*, 2310.

(26) Mislow, K.; Dougherty, D. A.; Hounshell, W. D. *Bull. Soc. Chim. Belg.* **1978**, *87*, 555 and references therein.

(27) The difference may indicate through-bond coupling of two anti phenyl groups in **1**. This point is under active investigation in our laboratories.

Table I. Relative Energies and Selected Structural Parameters of D_3 and S_6 Conformations of Hexaphenylethane (1) and Hexakis(2,6-di-*tert*-butyl-4-biphenyl)ethane (2) by EFF, MO, and X-ray Methods

method	$\Delta\Delta H_f^a$	D_3						S_6					
		r_c^b	r_r^c	ω_{pep}^d	ω_{eep}^e	ϕ_c^f	ϕ_r^g	r_c	r_r	ω_{pep}	ω_{eep}	ϕ_c	ϕ_r
Hexaphenylethane (1)													
AM ^h	-2.55 (-5.44) ⁱ	1.639	1.576	103.6	114.4	3.0	50.2	1.636	1.576	104.1	114.8	60.1	52.3
MMI ^{j,k}	-4.42	1.607	1.552	105.4	113.4	2.5	49.8	1.623	1.555	105.1	113.5	60.0	53.4
MMPI ^l	-2.01	1.631	1.552	106.7	112.2	3.1	50.8	1.602	1.547	106.3	112.4	60.0	55.1
MM2 ^{k,m}	-3.66	1.602	1.548	105.5	113.2	4.5	50.4	1.606	1.551	105.4	113.3	60.0	52.9
MNDO ⁿ	-2.57	1.681	1.570	106.2	112.6	9.7	51.1	1.682	1.569	106.2	112.5	60.0	53.7
Hexakis(2,6-di- <i>tert</i> -butyl-4-biphenyl)ethane (2)													
MMPI	-4.01	1.636	1.563	106.0	112.7	6.1	49.6	1.616	1.561	104.5	114.0	60.0	51.7
MM2	-6.31	1.630	1.557	104.9	113.7	6.4	48.7	1.635	1.568	103.8	114.7	60.0	48.5
X-ray ^o								1.474	1.621	105.8	115.7	58.4	56.7
									1.654	102.2	112.3	60.3	51.1
									1.622	104.9	114.8	61.3	54.9

^a $\Delta H_f(D_3) - \Delta H_f(S_6)$ in kcal mol⁻¹. ^b Central bond length in Å. ^c Cethane-C_{phenyl} bond length in Å. ^d C_p-C_e-C_p valence angle in degrees. ^e C_e-C_e-C_p valence angle in degrees. ^f C_p-C_e-C_e-C_p torsion angle (absolute value) in degrees. ^g C_e-C_e-C_p-C_{ortho} torsion angle (absolute value) in degrees. ^h Andose-Mislow force field, ref 16. Results taken from ref 4. ⁱ The hybrid AM-EHMO calculation, ref 6. ^j Allinger 1973 force field, ref 17. ^k Aromatic carbon atoms are treated "mechanically" by use of special stretch parameters. See text. ^l Allinger's MMI-VESCFMO calculation, ref 19. ^m Allinger 1977 force field, ref 20. ⁿ Dewar's semiempirical molecular orbital calculation by the MNDO approximation, ref 23. ^o Reference 8. Structural parameters were calculated on the basis of atomic coordinates supplied by courtesy of Dr. W. Winter.

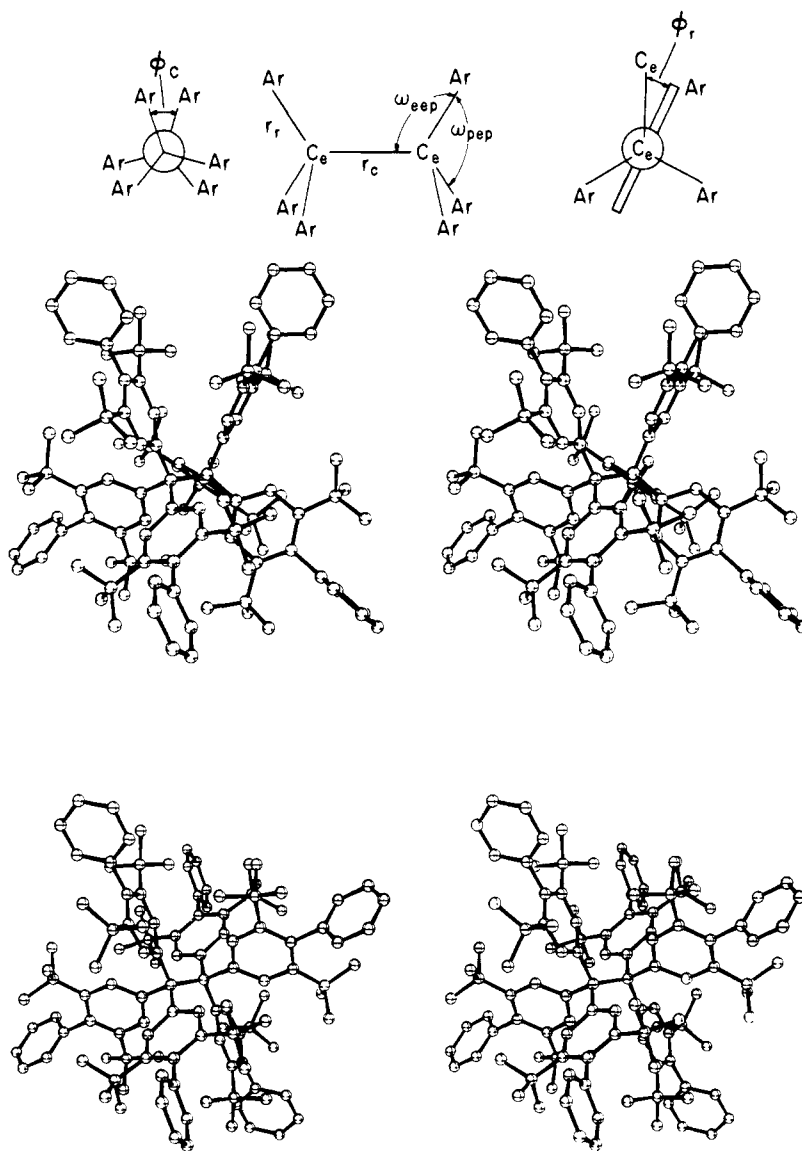


Figure 1. Stereoview of the calculated (MM2) minimum-energy structure of D_3 (top) and S_6 (bottom) conformations of hexakis(2,6-di-*tert*-butyl-4-biphenyl)ethane (2).

Table II. Calculated Deformation of Phenyl Rings in 1 and 2 As Given by Endocyclic C-C-C Torsion Angles (deg)

method ^a	D_3						S_6					
	1'-2'	2'-3'	3'-4'	4'-5'	5'-6'	6'-1'	1'-2'	2'-3'	3'-4'	4'-5'	5'-6'	6'-1'
Hexaphenylethane (1)												
AM	-2.6	1.2	0.5	-0.6	-1.1	2.5	-4.0	1.6	1.0	-0.8	-2.1	4.3
MMI	-1.4	0.5	0.5	-0.4	-0.6	1.5	-1.7	0.6	0.6	-0.6	-0.6	1.7
MMPI	-3.0	1.2	0.8	-0.8	-1.3	3.0	-3.9	1.6	1.2	-1.3	-1.4	3.9
MM2	-1.7	0.6	0.6	-0.5	-0.7	1.8	-1.9	0.7	0.7	-0.7	-0.7	1.9
MNDO	-2.4	0.9	0.8	-0.8	-0.9	2.4	-3.9	1.9	0.8	1.1	1.3	3.6
Hexakis(2,6-di- <i>tert</i> -butyl-4-biphenyl)ethane (2) (Inner Phenyl Rings)												
MMPI	-3.0	0.9	2.0	-2.3	-0.2	2.6	-4.7	5.7	-1.7	-2.6	3.8	-0.4
MM2	-2.3	0.9	0.6	-0.4	-1.2	2.5	-2.4	3.0	-0.9	-1.4	2.1	-0.4

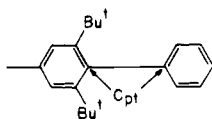
^a See footnotes of Table I for EFF and MO methods.Table III. Calculated C-C Bond Lengths (Å) in D_3 and S_6 Conformers of 2

bond	D_3		S_6	
	MMPI	MM2	MMPI	MM2
1-2	1.636	1.630	1.616	1.635
1-1'	1.563	1.557	1.561	1.568
1'-2'	1.399	1.397	1.400	1.399
2'-3'	1.405	1.402	1.408	1.404
3'-4'	1.417	1.412	1.414	1.413
4'-5'	1.416	1.411	1.414	1.411
5'-6'	1.404	1.401	1.405	1.402
6'-1'	1.402	1.399	1.406	1.402
4'-7'	1.522	1.522	1.518	1.522
7'-8'	1.401	1.401	1.400	1.401
8'-9'	1.397	1.396	1.398	1.397
9'-10'	1.398	1.397	1.398	1.397
10'-11'	1.399	1.398	1.399	1.398
11'-12'	1.398	1.397	1.398	1.397
12'-7'	1.400	1.400	1.400	1.401
3'-(1)	1.560	1.540	1.547	1.542
(1)-(2)	1.542	1.537	1.541	1.539
(1)-(3)	1.542	1.542	1.538	1.542
(1)-(4)	1.552	1.551	1.548	1.552
5'-(5)	1.558	1.540	1.550	1.546
(5)-(6)	1.545	1.545	1.541	1.539
(5)-(7)	1.552	1.552	1.550	1.558
(5)-(8)	1.543	1.537	1.538	1.540

latter represents EFF's which involve a "mechanical" treatment of aromatic rings.²⁸ To our knowledge, 2 ($C_{122}H_{150}$) is the largest molecule ever calculated by a full-relaxation EFF method.²⁴

We first ran the S_6 conformer of 2 on MMPI without any constraints. However, geometry optimization did not converge even after 27 CPU hours on a HITAC M-180 system, although the last structure was virtually identical with that of the energy

(28) In order to handle 2 by an EFF method with the "mechanical aromatic ring" approach, it is necessary to give a new atom type number and appropriate interaction parameters to the pivot carbon atoms (C_{pt}) of the biphenyl moiety. This task is complicated by the fact that such parameters depend on the dihedral angle between the two phenyl planes. In this particular case, however, the phenyl planes should remain practically perpendicular to each other because of the two ortho *tert*-butyl substituents. We used the following parameter set: Stretch $C_{pt}-C_{pt}$: k_s , 5.0 mdyne/Å, l_0 1.511 Å. Torsion $C_{pt}-C_{pt}-C_{pt}$: V_1 , -1.0, V_2 , 4.95, V_3 , 0.0 kcal mol⁻¹. The constants k_s and l_0 correspond to those in the MMPI scheme with p_{ij} equal to zero.^{19a} V_2 is taken from that of butadiene.^{19a} As a matter of fact, any combination of V_1 to V_3 can be assigned to our case, since we use only relative energies between conformers having almost identical geometries at the pivot bond, and the torsional energies at the pivot bond for the two conformers in question should vanish by taking the difference. Our tentative torsional function produces a flat minimum at the right dihedral angle, and the error in our relative energy calculation should therefore be minimal. In all other new parameters involving the atom C_{pt} used in the present calculation (a total of 20 sets), C_{pt} was taken as equivalent to C_{sp^2} .

Table IV. Calculated C-C-C Valence Angles (deg) in D_3 and S_6 Conformers of 2

angles	D_3		S_6	
	MMPI	MM2	MMPI	MM2
2-1-1'	112.7	113.7	114.0	114.7
1'-1-1''	106.0	104.9	104.5	103.8
1-1'-2'	124.7	122.9	124.8	123.7
1-1'-6'	122.4	122.9	123.4	122.8
2'-1'-6'	112.4	113.9	111.2	113.2
1'-2'-3'	126.9	125.3	127.1	125.3
2'-3'-4'	115.7	117.4	116.1	117.6
3'-4'-5'	122.3	120.7	121.9	120.6
4'-5'-6'	115.8	117.4	115.5	117.0
5'-6'-1'	126.8	125.3	127.8	126.0
3'-4'-7'	118.8	119.5	119.2	119.9
5'-4'-7'	118.9	119.7	118.9	119.5
4'-7'-8'	120.4	120.9	120.3	119.6
4'-7'-12'	120.3	118.6	120.4	119.8
12'-7'-8'	119.3	120.5	119.3	120.5
7'-8'-9'	120.6	119.8	120.5	119.8
8'-9'-10'	119.8	119.4	120.0	119.5
9'-10'-11'	119.9	121.0	119.8	120.9
10'-11'-12'	120.1	119.6	120.0	119.6
11'-12'-7'	120.2	119.7	120.4	119.6
2'-3'-(1)	118.3	117.4	118.1	117.6
4'-3'-(1)	126.0	125.3	125.8	124.7
3'-(1)-(2)	116.0	114.3	116.4	113.7
3'-(1)-(3)	107.2	107.7	107.9	108.6
3'-(1)-(4)	113.6	113.0	111.8	112.7
(2)-(1)-(3)	108.3	109.1	108.4	109.5
(2)-(1)-(4)	105.1	104.9	104.5	104.4
(3)-(1)-(4)	106.0	107.6	107.6	107.7
4'-5'-(5)	127.4	126.1	126.6	126.1
6'-5'-(5)	116.8	116.4	117.9	116.9
5'-(5)-(6)	118.4	115.4	117.7	114.5
5'-(5)-(7)	111.5	112.6	111.6	111.4
5'-(5)-(8)	106.5	106.8	107.3	108.7
(6)-(5)-(7)	104.4	104.4	104.0	103.9
(6)-(5)-(8)	106.7	108.5	107.5	109.1
(7)-(5)-(8)	109.0	108.9	108.3	109.0

minimum obtained by the method described below. The inefficiency in the final stage of optimization presumably arises either from extreme complexity of the energy hypersurface of such a large molecule, or from inadequacy of the diagonalization algorithm used in the Newton-Raphson minimization,¹⁸ or from both. Full utilization of symmetry constraints, even including hydrogen atoms, so that only one-sixth of the whole molecule (one 2,6-di-*tert*-butyl-4-biphenyl group and one of the ethane carbon atoms) could move independently, led smoothly to respective energy minima of D_3 and S_6 conformers with both force fields. Relative energies and salient structural features of the hexaphenylethane portion of 2 thus calculated are given in Tables I and II. Complete listings of calculated bond lengths, valence angles, and torsion angles of 2 are provided in Tables III-V. When the X-ray coordinates were used as input in the MM2 force field, energy minimization with the mechanical aromatic ring option stopped after 953 s CPU time and 246 iterations at an apparent local minimum. At this point the average internal

Table V. Calculated C-C-C Torsion Angles (deg) in D_3 and S_6 Conformers of **2**

torsion angle	D_3		S_6	
	MMPI	MM2	MMPI	MM2
1'-1-2-1'''	6.1	6.4	60.0	60.0
1'-1-2-1''	-113.9	-113.6	-60.0	-60.0
2-1-1'-2'	49.6	48.7	-51.7	-48.5
2-1-1'-6'	-138.9	-136.8	137.4	137.6
6'-1'-2'-3	2.6	2.5	-4.7	-2.4
1'-2'-3'-4'	-0.2	-1.2	5.7	3.0
2'-3'-4'-5'	-2.3	-0.4	-1.6	-0.9
3'-4'-5'-6'	2.0	0.6	-2.6	-1.4
4'-5'-6'-1'	0.9	0.9	3.8	2.2
5'-6'-1'-2'	-3.0	-2.3	-0.4	-0.4
3'-4'-7'-8'	-92.0	-92.5	-83.7	-83.4
3'-4'-7'-12'	88.3	87.4	96.6	96.8
5'-4'-7'-8'	90.4	89.9	95.3	95.5
5'-4'-7'-12'	-89.3	-90.1	-84.5	-84.3
12'-7'-8'-9'	-0.4	0.0	-0.3	-0.2
7'-8'-9'-10'	0.0	0.0	-0.1	0.0
8'-9'-10'-11'	0.3	0.0	0.3	0.1
9'-10'-11'-12'	-0.2	0.0	-0.1	0.0
10'-11'-12'-7'	-0.3	0.0	-0.3	-0.2
11'-12'-7'-8'	0.3	0.0	0.5	0.3
2'-3'-(1)-(2)	-147.7	-152.9	153.0	151.9
2'-3'-(1)-(3)	91.1	85.7	-84.9	-86.0
2'-3'-(1)-(4)	-25.8	-33.0	33.1	33.3
4'-3'-(1)-(2)	34.3	30.1	-28.5	-30.3
4'-3'-(1)-(3)	-86.9	-91.3	93.5	91.9
4'-3'-(1)-(4)	156.2	150.0	-148.4	-148.9
4'-5'-(5)-(6)	105.2	99.3	-20.2	-23.3
4'-5'-(5)-(7)	-136.1	-141.2	-140.2	-140.9
4'-5'-(5)-(8)	-14.9	-21.4	101.2	98.9
6'-5'-(5)-(6)	-72.7	-77.5	159.1	156.3
6'-5'-(5)-(7)	46.1	42.0	39.1	38.7
6'-5'-(5)-(8)	167.2	161.8	-79.5	-81.4

coordinates of the molecule were: $r_c = 1.628 \text{ \AA}$, $r_r = 1.563 \text{ \AA}$, $\omega_{\text{pp}} = 103.77^\circ$, $\omega_{\text{ep}} = 114.71^\circ$, $\phi_c = 60.0^\circ$, $\phi_r = 50.94^\circ$. It is evident that here, as well as in the MMPI minimization, even partial relaxation of the X-ray structure yields bonding parameters closely similar in all essential respects to those calculated for the constrained minimum structure of S_6 -**2** (cf. Table I).

Consistent with the results of our calculations on **1**, the D_3 conformer of **2** was calculated to be more stable than the S_6 form by 4–6 kcal mol⁻¹. This result has direct bearing on the question of why the S_6 , instead of the D_3 , conformer is found in the crystal. As was noted above, lattice forces might be held responsible for the discrepancy between the S_6 conformation found in the crystal and the D_3 ground state calculated for the free molecule. The calculated molar energy difference is very small, given the enormous size of this molecule and the correspondingly small fractional van der Waals contact between the molecule and its surroundings, and corresponds to a conformational energy difference of merely ca. 1 kcal mol⁻¹ for a conventionally sized molecule such as biphenyl. It is therefore quite reasonable to ascribe the observed conformational reversal to a crystal-packing effect.¹⁰

The most important conclusion emerging from our EFF calculations is that *the tert-butyl groups have no special effect on the bonding parameters of 2*. Though the *tert-butyl* groups are crowded, the 272 atoms of **2** are all located in reasonable positions

in the molecule (see Figure 1 for carbon framework). The bonding parameters in the hexaphenylethane portions of both conformers of **2** differ in no significant respect from the corresponding parameters in **1** (Table I), and the central bond is again calculated to be slightly in excess of 1.6 Å. The only notable, though relatively trivial, contrast between **1** and **2** concerns the deformation of the inner phenyl rings (the outer rings are practically planar). Whereas the rings in the D_3 conformer assume a slight "twist-boat" conformation, as in **1**, those of the S_6 form assume a slight "twist" form (Table II). Except for this point, the hexaphenylethane portions of **2** can be regarded as almost superimposable on the corresponding conformers of **1**.

Conclusion

Three major conclusions emerge from this study. First, our previous conclusions⁴ concerning the structure of **1** have been fully confirmed. Indeed, the EFF-calculated central bond length of 1.60–1.64 Å should be considered a lower limit, for there is no reason to dismiss the possibility of a bond length close to 1.68 Å, as calculated by MNDO for **1**.^{7,25}

Second, our calculations show that the observed⁸ S_6 symmetry of **2** in the crystal is readily accounted for by packing forces in the solid state, and is in no sense contradictory to the calculation of a D_3 ground state for **1** and **2**.

Third, our calculations have failed to uncover any special steric effects operating in **2** which might serve to reconcile the extraordinary discrepancy between the calculated (1.616 (MMPI), 1.635 (MM2) Å) and found⁸ (1.474 Å) central C–C bond lengths, and the somewhat lesser, but still serious, discrepancy between the calculated (1.561 (MMPI), 1.568 (MM2) Å) and found⁸ (1.621, 1.654, 1.622 Å) C_{ethane}–C_{phenyl} bond lengths. We are not aware of any electronic effect which could account for discrepancies of this magnitude.²⁹ It is therefore tempting to conclude that the abnormally short central bond length in the reported⁸ X-ray structure of **2** is grossly in error,¹¹ and that consequently other reported⁸ structural parameters, i.e., the C_{ethane}–C_{phenyl} bond lengths, also require revision. We hasten to add, however, that the alternative conclusion is by no means excluded, i.e., that a novel bond shrinkage effect is operative in **2**, and by implication in **1**, which is not taken account of in the parametrization of any of the computational schemes employed in the present and previous⁴ studies. The chemical implications of this last alternative are of major importance, and a reinvestigation of the X-ray structure of **2** is therefore clearly called for.

Acknowledgment. We thank Dr. W. Winter for atomic coordinates of **2**, Drs. D. A. Dougherty, W. D. Hounshell, and J. P. Hummel for preliminary calculations, and Professor H.-B. Bürgi for a helpful discussion. The work at Hokkaido University was supported by a Grant-in-Aid for Scientific Research (No. 447016) from the Ministry of Education, Science and Culture, and the work at Princeton University by the National Science Foundation (CHE-8009670). Calculations were performed at the Computer Centers of Hokkaido University and the Institute for Molecular Science.

(29) In the closely related case of 9,9'-bitriptycyl, the experimental value³⁰ of the central bond length (1.558 (3) Å) is well reproduced by the MM2 EFF (1.552 Å), and somewhat overestimated by AM EFF (1.589 Å)³⁰ and MNDO (1.597 Å) calculations.

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