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ENERGY-MINIMUM STRUCTURE OF THE HYDROCARBON PORTION OF $[4_5]$(1,2,3,4,5)FERROCENOPHANE

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ABSTRACT

In order to assist in the interpretation of the D_{5h} molecular structure of $[4_5]$(1,2,3,4,5)ferrocenophane (**1**) obtained from x-ray crystallographic analysis, a hypothetical hydrocarbon $C_{30}H_{40}$ (**2**) was derived from **1** by removing the iron atom and subjected to geometry optimization by molecular mechanics. A stable D_5 conformer was found for **2**, which has a $g^+g^-g^+$ helical bridge conformation and a ring–ring distance almost identical with that in **1** and ferrocene itself. Optimization of a perhydrogenated hydrocarbon model gave a highly strained C_1 structure.

INTRODUCTION

We have previously reported the first synthesis of $[4_5]$(1,2,3,4,5)ferrocenophane (superferrocenophane) (**1**).[1,2] The x-ray determination of the structure of **1**[1] offered intriguing problems: the molecular structure is effectively D_{5h} [Strictly, the x-ray diffraction data for **1** were solved on the assumption of C_2 symmetry (see Table 2).[1] According to the x-ray analysis, three bridges are nearly linear (all very approximately *syn*) but two bridges are composed of three synclinal arrangements] resembling 'a beachball squashed in at the both ends,'[3] and having remarkably large anisotropic thermal vibration at C_β and $C_{\beta'}$ with major axes of vibration in equatorial directions and abnormally short $C_\alpha—C_\beta$ and $C_\beta—C_{\beta'}$ bond lengths (Tables 1 and 2). NMR spectra of **1** gave only three ^{13}C signals and two broad proton peaks at room temperature. The possibility of rapid conformational interconversion among unspecified conformers has been suggested.[1]

The molecule is not suited for study with conventional molecular models: congestion between bridges is so exaggerated with CPK space-filling model that it is hardly possible to construct

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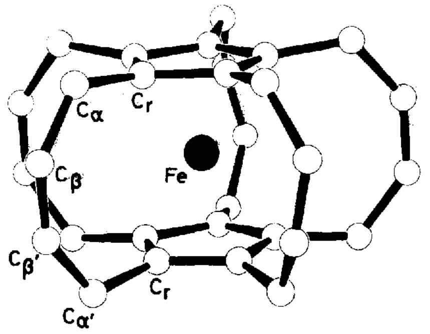


1, (D_{5h})

the molecule. Even though the model could somehow be assembled by brute force, the bridge atoms are so tightly packed that the bridges do not flip at all. Hence we decided to perform a computational search of potential conformations which should be hidden behind the experimental observations.

COMPUTATIONAL TECHNIQUE

The lack of parameters for ferrocenyl iron in the available empirical and semi-empirical computational methods excluded the possibility of making calculations on the molecule **1** as it is. Simple removal of the iron atom from **1** gives a hypothetical cage hydrocarbon **2** ($C_{30}H_{40}$), with two five-membered rings consisting only of sp^2 carbon atoms. Although the neutral molecule **2** may look unusual as a chemical entity, it is used here as a model for studying the steric features of **1**, which are our present concern. The model **2** could be directly subjected to MMP2[4] calculation [Program MMP2(82) was obtained from QCPE]. In MM2′[5] calculations (parameters pertaining to the sp^2 carbon atom are transferred from MM2), the ring carbon atoms were treated mechanically as is often practised in molecular mechanics calculations on benzene derivatives[6] [An improved force field (MM3) for this purpose has recently been proposed[7]], except for the natural bond length within the five-membered ring, which was set at 1·440 Å, the C_r—C_r distance in gaseous ferrocene.[8]

In AM1[9] calculations [a locally updated version of MOPAC (version 3.00) was used[10]], the iron atom was removed but the cyclopentadienyl anion rings were retained in order to realize the closed-shell electron configuration and a sparkle[11] with double positive charge was placed at the centre of the molecule in order to neutralize the charges (**3**). We first optimized the structure without any constraint and obtained an energy-minimum structure in which the inter-ring distance was too large (4·42 Å compared with the x-ray value of 3·22 Å)[1] and the α-carbon atom on the bridge deviated from the cyclopentadienyl ring plane in the *endo* direction, in contrast to **1**, where C_α deviates in the *exo* direction. Clearly, the formal charge of +2 in the sparkle was not sufficient to simulate the bonding of the Fe^{2+} ion with the cyclopentadienyl rings in **1**. We then naively kept the inter-ring distance of **3** at 3·224 Å and optimized the structure, but this measure still proved unsatisfactory, as mentioned below.

The structures shown were drawn by the use of an ORTEP program.[12] Vibrational frequencies were calculated by using the BIGSTRN3 program.[13]

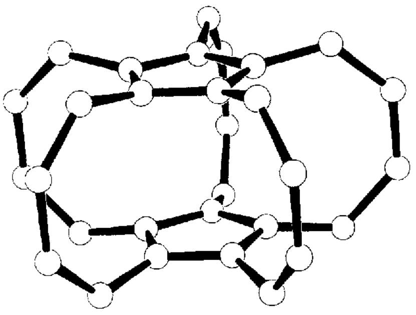
RESULTS AND DISCUSSION

Energy-minimum confrontation

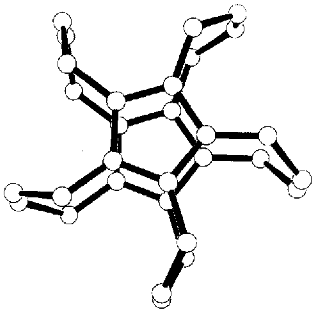
All three computational methods employed here failed to minimize the structures of **2** and **3** when D_{5h} (e.g. **2a**), C_{5h} (**2b**) and C_5 (**2c**) symmetries were imposed (structures **3a**, **3b** and **3c** are not reproduced here), but readily produced D_5 structures as energy minima. Figure 1 illustrates the structure (**2d**) obtained with MM2′. Constrained AM1 calculation on **3** also gave a well defined D_5 conformer (**3d**, Table 1). Although AM1 gave a d value (0·151 Å) closest to the observed value (0·147 Å), the $\mathrm{C_r}$—$\mathrm{C_r}$ distance came out too long. The reason for this bond elongation is apparently the fixation of the inter-ring distance: in order to reduce the too strong electrostatic repulsion between the two cyclopentadienyl rings at this distance, the rings simply expanded. The calculated heat of formation of **3d** is fairly high. The model **3** is hence concluded to be unsuitable for the present study.

The remaining D_5 structures **2d**, as obtained by molecular mechanics (first and second columns in Table 1) gave d and D values which are surprisingly close to the x-ray values for **1**, possibly suggesting an overwhelming role of the straining tetramethylene bridges in determining the steric features of **1**. We use MM2′ hereafter instead of MMP2 in view of the better agreement of MM2′-calculated d and D with experimental values and also because of shorter computation time of MM2′ compared with MMP2.

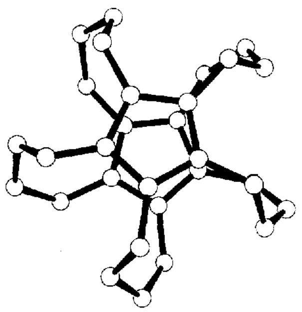
The MM2′ structure of **2d** is indeed a 'good' one, having no unusual interatomic distances and valence angles, and a very low steric energy (27·9 kcal mol^{-1}) for such an apparently highly congested molecule. The dominant contributor to the total steric energy is the angle bending



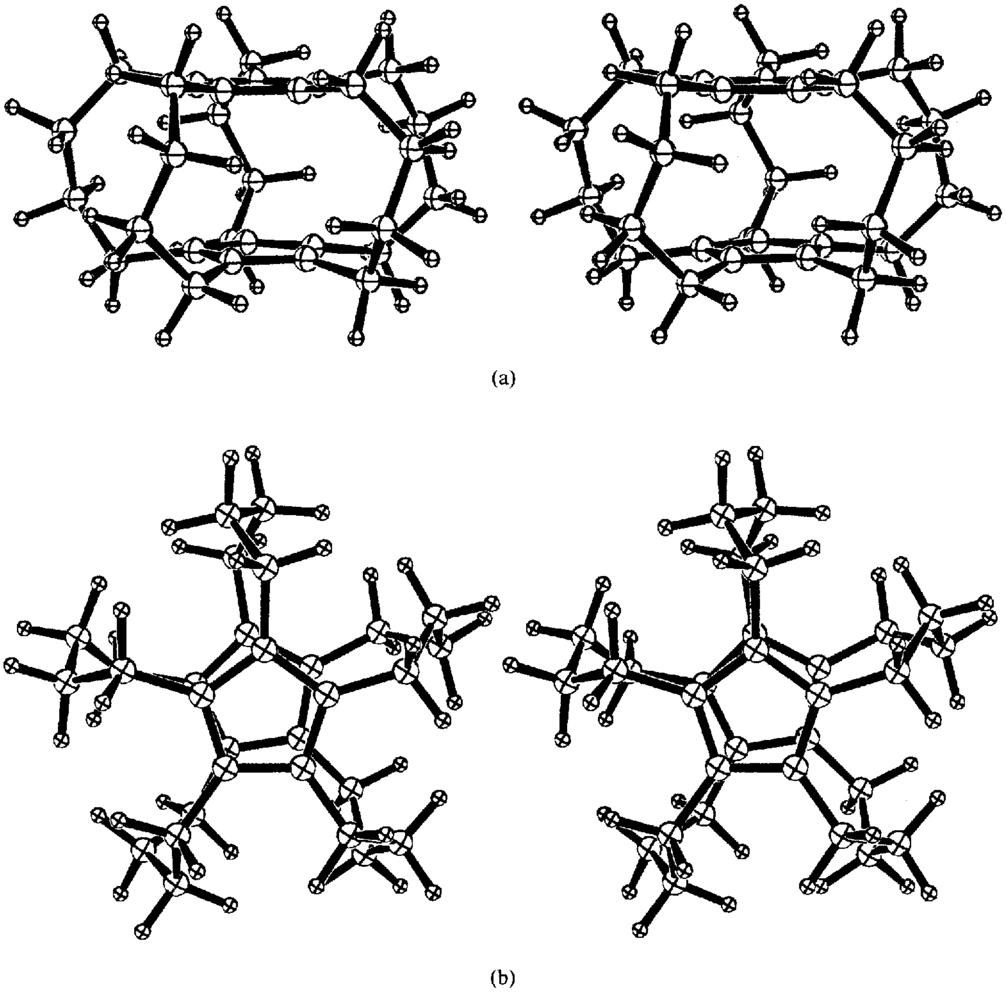
2a, D_{5h}



2b, C_{5h}

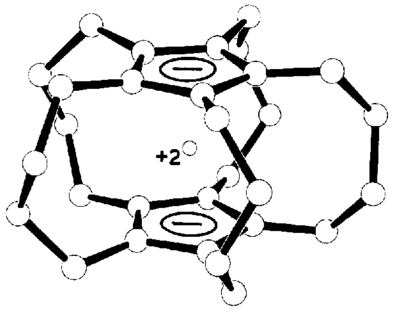


2c, C_5


(a)

(b)

Figure 1. ORTEP stereo drawing of the D_5 conformer (**2d**) of the hydrocarbon portion ($C_{30}H_{40}$) of **1**. (a) Side view; (b) top view



3d, D_5

Table 1. Structures and energies of hydrocarbon models (**2** and **3**) of [4]superferrocenophane (**1**) and its perhydrogenated product (**4**)[a]

	$C_{30}H_{40}$					$C_{30}H_{50}$
	2d	**2d**	**2e**	**2f**	**3d**	**4**
Method:	MM2′	MMP2	MM2′	MM2′	AM1[b]	MM2′[c]
Point group:	D_5	D_5	C_2[d]	D_{5h}[e]	D_5	C_1
$C_r—C_r$	1·450	1·419	(1·430)	1·450	1·475	1·563
$C_r—C_\alpha$	1·503	1·507	(1·512)	1·497	1·478	1·552
$C_\alpha—C_\beta$	1·535 (1·482)[f]	1·539 (1·475)[f]	(1·436)	1·537	1·524	1·539
$C_\beta—C_{\beta'}$	1·535 (1·354)[f]	1·539 (1·364)[f]	(1·324)	1·542	1·517	1·531
d[g]	0·210	0·315	(0·147)	0·225	0·151	−0·609
D[h]	3·097	2·844	(3·224)	(3·224)	(3·224)	5·197
$C_r—C_\alpha—C_\beta—C_{\beta'}$	−67·9	−63·4	(0·0)	0·0	−70·3	—
$C_\alpha—C_\beta—C_{\beta'}—C_{\alpha'}$	94·8	90·4	(0·0)	0·0	99·3	—
$C_{\beta'}—C_\beta—C_\alpha—C_r$	−67·9	−63·4	(0·0)	0·0	−70·3	—
ω[i]	−8·4	−8·0	(−1·3)	0·0	−7·0	8·3
Stretch	1·11	2·45	128·68	1·45		7·82
Bend	36·11	36·85	169·14	143·02		102·21
Stretch–bend	0·30	0·85	−19·57	1·33		3·93
van der Waals:						
1,4-	9·70	16·74	34·40	21·24		38·99
Other	−15·14	−7·54	−17·73	−12·31		−1·70
Torsion	−5·71	−5·38	−1·10	19·90		69·42
Dipole	1·54	1·66	1·52	1·51		0·00
Total energy	27·91	45·63	295·34	176·14	(154·39)[j]	220·67
$\nu_{\min}$[k]	109·8	—	—	—	—	112·1

[a] Distances in Å, angles in degrees, steric energies in kcal mol^{-1} and vibrational frequencies in cm^{-1}.

[b] Optimized with a double-positive-charged sparkle in the centre of the molecule and the inter-ring distance D constrained to the x-ray value.

[c] Averaged distances given.

[d] Coordinates of carbon atoms fixed to the x-ray structure and the hydrogen atoms optimized. The structural parameters given in this column in parentheses are the average of x-ray values, which are given in full in Table 2.

[e] Optimized with the inter-ring distance D constrained to the x-ray value.

[f] Distance between average positions of atoms undergoing presumed anisotropic motions of bridges along the direction perpendicular to the plane defined by, e.g. C_r, C_r, and the midpoint of C_β and $C_{\beta'}$ (see Structure **1**).

[g] Deviation of α-carbon atom on the bridge from the ring plane. Positive for *exo* bending and negative for *endo*

bending.

[h] Distance between two Cp rings or two cyclopentane rings.

[i] Ring-ring twist angle.

[j] Heat of formation.

[k] Lowest vibrational frequency calculated by using BIGSTRN3 program.[13]

term (see the lower half of Table 1). About half of the bending strain (18·2 kcal) arises from the intra-ring Cr—Cr—Cr angle (108·0°), which deviates considerably from the natural angle for the sp^2-hybridized carbon. The remainder of the angle strain comes from the $C_r—C_\alpha—C_\beta$ (118·3°) and $C_\alpha—C_\beta—C_{\beta'}$ (116·8°) angles. It is interesting that the sizable van der Waals repulsion, arising mostly from the *gauche* 1,4-H–H interactions across the $C_\beta—C_{\beta'}$ units and from the close H–H contacts between neighbouring bridges, almost vanishes owing to the attractive van der Waals interactions acting over longer distances within the molecule. The torsional strain is fairly small because of the well staggered bridge conformation.

The D_{5h} structure **2a**, a naive model for the hydrocarbon portion of the x-ray structure of **1**, was subjected to further scrutiny with MM2′ in order to compare it with **2d**. First, the carbon atomic coordinates were fixed to the x-ray coordinates (C_2 symmetry) while the attached hydrogen atoms were allowed to relax (**2e**, third column in Table 1). Second, the whole structure was optimized while imposing the D_{5h} constraint on the carbon skeleton and fixing the distance D at the x-ray value (**2f**, fourth column of Table 1). These calculations gave a 270 and 150 kcal mol^{-1} higher steric energy, respectively, compared with the D_5 structure **2d**. The D_{5h} structure now assumed normal C—C bond lengths but the C—C—C angles along the bridge became too large to be realistic. Hence it is highly unlikely that the D_{5h} structure exists.

Further considerations on the MM2′-calculated D_5 structure (2d)

This structure is chiral, with six helical axes as the stereogenic elements, one passing through the centres of five membered rings and five along every tetramethylene bridge. The two five-membered rings are slightly skewed along the first axis (ω, Table 1), whereas they are virtually eclipsed in the x-ray structure. There is a possibility that the observed eclipsing may be the result of averaging over a pair of enantiomers that may be interconverting into each other (see below). The tetramethylene bridges $C_r—C_\alpha—C_\beta—C_{\beta'}—C_{\alpha'}—C_r$ involves three dihedral angles of the type C—C(sp^3)—C(sp^3)—C, and these angles are arranged in the $g^-g^+g^-$ sequence with the both *gauche* ends identical with respect to the sign and magnitude. This bridge conformation corresponds to a short right-handed (P) helix. The conformation of **2d** can be adequately expressed by helicity alone; hence the particular conformer given in Table 1 can be designated as m-PPPPP (m indicating the negative sign of the skew angle between the two five-membered rings). There should exist an enantiomer of this conformer, with the bridge conformation in $g^+g^-g^+$, which can be designated as p-MMMMM.

The x-ray and NMR observations with **1**, as mentioned initially are compatible with rapid interconversion between the enantiomeric pair, m-PPPPP $\rightleftharpoons$ p-MMMMM, in both the solid and solution at room temperature on the experimental time scale. The possibility of static disorder in the crystal, namely a racemic mixture of m-PPPPP and p-MMMMM conformers occupying the same crystal sites at random, still remains. Although the NMR observations indicate rapid conformational interconversion in solution, there is at present no direct evidence that denies the static disorder in the crystal. Hence an anisotropic displacement probability analysis[14,15] of the x-ray data is clearly desirable and we are planning to apply it to the x-ray data of **1**.

If one assumes that the interconversion involves only the flipping of C_β and $C_{\beta'}$ carbon atoms of tetramethylene bridge and these motions are perpendicular to a plane defined by the two opposing ring carbon atoms (C_r) and the midpoint of C_β and $C_{\beta'}$, then the average C—C bond lengths involving C_β and $C_{\beta'}$ atoms can be estimated from the projections of these carbon atoms on to this plane. The 'averaged' bond distances thus estimated are given in

Table 2. Salient x-ray structural features of superferrocenophane (**1**)[a]

	Bridge No.				
	1	2	3	4	5
$C_r—C_r$	1·409	1·420	1·456	1·434	1·432
$C_r—C_\alpha$	1·511	1·530	1·497	1·516	1·508
$C_\alpha—C_\beta$	1·421	1·462	1·436	1·431	1·431
$C_\beta—C_{\beta'}$	1·337	1·357	1·286	1·287	1·357
$C_r—C_\alpha—C_\beta—C_{\beta'}$	−12·3	−39·2	−1·1	−1·2	−33·2
	−12·3	−33·2	−1·2	−1·1	−39·2
$C_\alpha—C_\beta—C_{\beta'}—C_{\alpha'}$	16·5	53·8	0·9	0·9	53·8

[a] Distances in Å, angles in degrees. Calculated from the atomic coordinates in the supplementary material in Ref. 1.

parentheses for **2d** in Table 1 and they agree reasonably well with the observed values (Table 2; see also **2e** in Table 1).

What will be the mechanism of dynamic disorder? If all the bridges rotate simultaneously in the conformational interconversion, the D_{5h} structure **2f** will be very close to the transition state. However, the high computed potential energy of **2f** renders this assumption highly unlikely. Less concerted or even step-by-step inversion processes seem more likely. However, further computational work on the stereodynamics of **2** was suspended at this point until we are able to handle **1** itself by computational means (work to parameterize MM2′ for ferrocene is in progress in our laboratories).

Hydrogenation of 1

Using the powerful MM2′, we attempted to hydrogenate **2** in the computer to obtain some information on the experimental possibility of hydrogenating **1**. This task proved difficult. After numerous failures, an asymmetric (C_1), energy-minimum structure of $C_{30}H_{50}$ hydrocarbon **4** (hexacyclo[$18.5.5.0^{2,13}.0^{7,21}.0^{8,19}.0^{14,26}$]triacontane), was obtained (Figure 2)

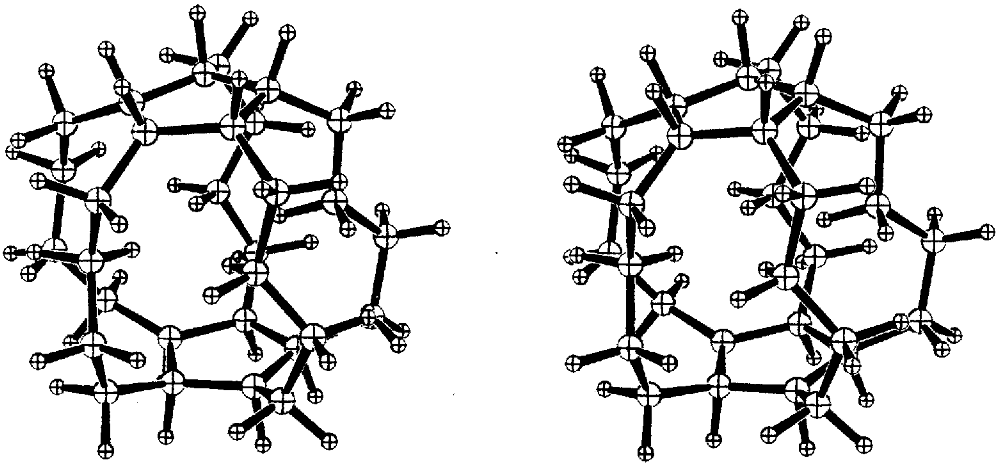
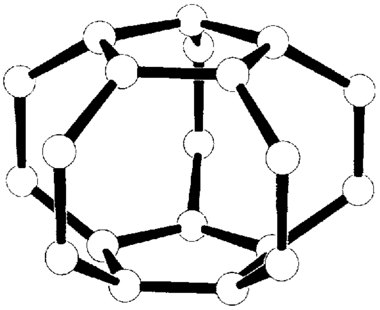
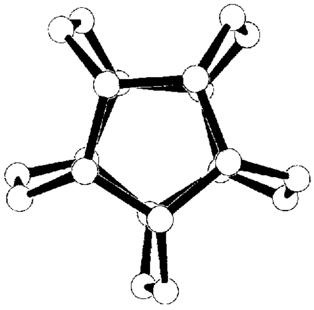


Figure 2. ORTEP stereo drawing of an asymmetric energy-minimum structure of perhydrogenated model $C_{30}H_{50}$ (**4**)

starting from an AM1-minimized structure of **3**. (One of the earlier results from AM1 calculations on **3**, having D_5 symmetry and a negative d value, was used to attach hydrogen atoms *exo* to the ring.) In this structure, however, four of the five bridges have one of the C—H bonds pointing to the inside of the cage, which would have been impossible in the presence of the iron atom. The total steric energy of **4** is 221 kcal mol^{-1} (last column in Table 1) and a number of abnormal angles are present (e.g. ca 120° for $C_r—C_\alpha—C_\beta$ and ca 125° for $C_r—C_r—C_\alpha$).



5, D_{5h}



5, D_5

It is interesting to note here that reasonable structures are available for a lower homologue **5** (hexacyclo[12.3.3.0^{2,9}.0^{5,20}.0^{6,13}.0^{10,17}]icosane). According to Ermer[16] who used CFF, the ethano-bridged **5** could be optimized to a D_5 energy minimum. Ermer stated that the eclipsed conformation D_{5h} is only 4·72 kcal mol^{-1} less stable than D_5 and is a one-dimensional partial energy maximum which directly connects the enantiomeric pair of the energy-minimum D_5 conformer on the torsional energy surface of **5**. In these conformations of **5**, $C_r—C—C$ angles are highly opened to about 122°. We confirmed Ermer's results, using MM2′: the saddle point conformer (D_{5h}) is 3·64 kcal mol^{-1} above the energy minimum (D_5).

These results suggest that the hydrogenation of **1** with five tetramethylene bridges must produce tremendous steric strain among the bridges, whereas the strain may be reduced if the bridges were shorter. Numerous attempts to hydrogenate **1** under various conditions have so far been unsuccessful.

CONCLUSIONS

The D_5 conformer **2d** of the hydrocarbon model of **1** has surprisingly unstrained arrangements of well staggered, helical tetramethylene bridges and it appears to be a potential candidate for the structure of the hydrocarbon portion of **1**. The *exo* bending of bonds extending from the ferrocene ring and the inter-ring distance of **1** could be quantitatively reproduced by molecular mechanics, but not by AM1, on the model **2**. It is likely that the structural features of **1** are dominated by the steric requirements arising from the closely packed tetramethylene bridges.

The observed x-ray results for **1** are compatible with a picture in which the enantiomeric conformers of **2d**, m-PPPPP and p-MMMMM, coexist, thus causing static or dynamic disorder in the crystal. If m-PPPPP and p-MMMMM conformers interconvert rapidly at room temperature, the saddle point cannot be of the D_{5h} symmetry. Hydrogenation of **1** must be difficult.

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REFERENCES

1. M. Hisatome, J. Watanabe, K. Yamakawa and Y. Iitaka, *J. Am. Chem. Soc.* **108**, 1333 (1986).
2. A. Nickon and E. F. Silversmith, *Organic Chemistry: the Name Game, Modern Coined Terms and Their Origins*, p. 211. Pergamon Press, New York (1987).
3. *Chem. Eng. News* **64**, (14), 16 (1986).
4. J. T. Sprague, J. C. Tai, Y. Yuh and N. L. Allinger, *J. Comput. Chem.* **8**, 581 (1987).
5. C. Jaime and E. Ōsawa, *Tetrahedron* **39**, 2769 (1983).
6. N. L. Allinger, *QCPE Bull.* **3**, 32 (1983).
7. N. L. Allinger and J.-H. Lii, *J. Comput. Chem.* **8**, 1146 (1987).
8. A. Haaland and J. E. Nilsson, *Acta Chem. Scand.* **22**, 2653 (1968).
9. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
10. M. Togasi, J. M. Rudziński, Z. Slanina, E. Ōsawa and T. Hirano, *QCPE Bull.* **7**, 8 (1987).
11. MOPAC Program Manual, *QCPE* 464.
12. C. K. Johnson, *ORTEP-II: A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations.* Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN (1976).
13. R. B. Nachbar, Jr, and K. Mislow, *QCPE* 514.
14. J. D. Dunitz, V. Schomaker, K. N. Trueblood, *J. Phys. Chem.* **92**, 856 (1988).
15. J. D. Dunitz, C. Krüger, H. Irngartinger, E. F. Maverick, Yu Wang and M. Nixdorf, *Angew. Chem., Int. Ed. Engl.* **27**, 387 (1988).
16. O. Ermer, *Aspekte von Kraftfeldrechnungen*, p. 386. Wolfgang Baur, Munich (1981).