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## Stereochemical Analysis of 1,1,2,2-Tetraarylethanes.

### 1. Static Stereochemistry

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**Abstract:** Empirical force field calculations on 1,1,2,2-tetraphenylethane (TPE) and 1,1,2,2-tetrakis(2,6-xylyl)ethane (TXE) show that these molecules adopt a  $C_2$  ground-state conformation in which the methine hydrogens are in anti positions. The dihedral angles of all four rings are equally signed; these systems can therefore be viewed as four-bladed molecular propellers. Comparison of the geometric parameters for TPE and TXE reveals that TXE is a highly strained molecule, as demonstrated by the unusual elongation of the central C-C bond and the unusual enlargement of the central C-C-C angles. The  $^1H$  NMR spectra of tetramesitylethane (TME) and 1,2-dimesityl-1,2-bis(2,4,6-trimethoxyphenyl)ethane (**2**) at the slow exchange limit are also consistent with a  $C_2$  conformation in solution. The racemic and meso forms of **2** have been separated and configurations have been assigned to the two stereoisomers on the basis of their NMR spectra. Treatment of the static stereochemistry of 1,1,2,2-tetraarylethanes in terms of a group theoretical approach leads to a description of the full permutation-inversion group, to the calculation of the number of isomers for any given substitution pattern in such systems, and to the recognition of systems which are stereochemically correspondent to 1,1,2,2-tetraarylethanes.

In continuation of our recent investigations dealing with the static and dynamic stereochemistry of molecules possessing two or more aryl groups attached to a central atom,<sup>2</sup> we extended our field of inquiry to the more complex 1,1,2,2-tetraarylethane system, in which *two* central atoms each bear a complement of aryl groups. Such systems have been investigated in the past, notably in conjunction with the radical dissociation process,<sup>3</sup> the pinacol-pinacolone rearrangement,<sup>4</sup> ethane rotation barriers,<sup>5</sup> and conformer determination with regard to the central ethane bond.<sup>5,6</sup> However, the ground-state geometry and conformational dynamics of 1,1,2,2-tetraarylethanes have so far received little attention, and the present work was initiated in order to provide a deeper insight into these problems.

#### Ground-State Conformation of Tetraarylethanes

**The Anti Conformation.** In 1,1,2,2-tetraarylethanes (hereafter simply referred to as tetraarylethanes), the ethane torsional angle represents an additional variable parameter which is not present in systems containing aryl rings attached to only one central atom. Previous reports dealing with dipole moment measurements on tetraarylethanes<sup>6</sup> and 1,2-dichloro-1,1,2,2-tetraphenylethane<sup>5</sup> have concluded that the most stable rotamer is the one in which the methine hydrogens or chlorines are in anti (trans) positions.

In order to obtain more detailed information, we turned to empirical force field calculations (molecular mechanics).<sup>2h,7</sup> Our calculations, which will be fully described in a later section, reveal that in 1,1,2,2-tetraphenylethane (TPE), the energy content of the least strained gauche rotamer is ca. 5 kcal/mol above that of the anti form, whence it follows that the equilibrium population of the gauche rotamers is vanishingly small as compared to that of the anti form. This energy difference can be expected to be even greater for bulkier aryl groups, and consequently we can generalize our conclusion that only those

staggered rotamers are significantly populated in the ground state in which the methine hydrogens occupy the anti positions.

**Orientation Capabilities of the Aryl Rings.** The most symmetric structure for a tetraarylethane in the anti conformation is one possessing  $C_{2h}$  symmetry. This symmetry imposes constraints on the relative values of the four dihedral angles ( $\phi$ ) which describe the orientations of the four aryl rings, and which are defined by the four atoms joined by the three bonds leading from a methine hydrogen to an ortho benzene carbon atom ( $H-C_{\text{ethane}}-C_{\text{aryl}}-C_{\text{ortho}}$ ). For example, in 1,1,2,2-tetrakis(2,6-xylyl)ethane (TXE, Figure 1) these angles are  $H1-C1-C2-C3$ ,  $H1-C1-C8-C9$ ,  $H1'-C1'-C2'-C3'$ , and  $H1'-C1'-C8'-C9'$ . The sign of the dihedral angle is defined as positive if, looking down the  $C_{\text{ethane}}-C_{\text{aryl}}$  bond axis (e.g.,  $C1-C2$ ) from the ethane carbon atom ( $C1$  or  $C1'$ ), a counterclockwise rotation of the aryl group is required to eclipse the nearest  $C_{\text{aryl}}-C_{\text{ortho}}$  (e.g.,  $C2-C3$ ) and  $H-C_{\text{ethane}}$  (e.g.,  $H1-C1$ ) bonds ( $\phi = 0^\circ$ ). Thus, dihedral angles ranging from  $-90$  to  $+90^\circ$  suffice to describe all of the possible orientations for an aryl ring possessing a local  $C_2$  axis. In the ground state of TXE, all four dihedral angles are of the same sign (negative for the enantiomer depicted in Figure 1). On the other hand, if a ring lacks a local  $C_2$  axis, values ranging from  $-180$  to  $+180^\circ$  are required to describe all possible orientations.

Desymmetrization of the  $C_{2h}$  structure results in forms with  $C_s$ ,  $C_i$ ,  $C_2$ , and  $C_1$  symmetry (the subgroups of  $C_{2h}$ ) and is accomplished by removing at least two of the three nontrivial symmetry elements ( $C_2$ ,  $\sigma$ ,  $i$ ) in the  $C_{2h}$  form. In Figure 2 are depicted representative structures which belong to these various point groups; note that there are no constraints on the value of each individual  $\phi$  within each point group, and that an infinite number of conformations are therefore possible within each class.

In principle, tetraarylethanes can exist in conformations belonging to any one of the symmetries described above.

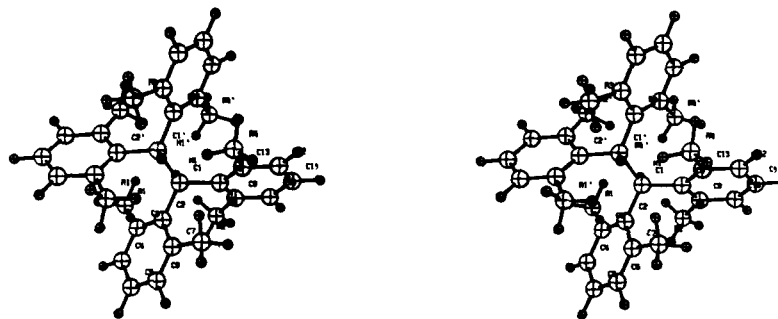


Figure 1. ORTEP stereoview of TXE in the  $C_2$  conformation. Atom labeling scheme is indicated. R =  $\text{CH}_3$ .

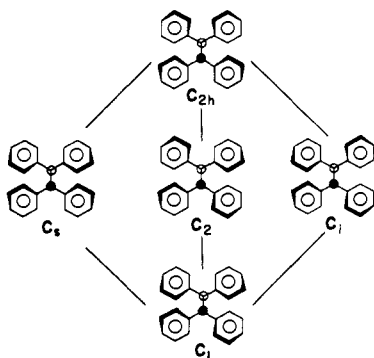


Figure 2. Point group lattice for TPE in the anti conformation.

However, there now exists a fairly impressive body of evidence<sup>2</sup> that whenever two or three aryl rings are attached to a central atom, and provided that these aryl rings have local  $C_2$  axes (or that the substituents on the two edges of the phenyl rings are not grossly different in steric requirement), the sense of twist of the aryl rings is the same; i.e., the conformation is that of a molecular propeller.<sup>2c</sup> We shall therefore make the simplifying assumption (which, as will be shown, is vindicated by experimental evidence) that for tetraarylethanes, whose rings are balanced in that the two ortho substituents on each phenyl ring do not differ appreciably in steric size, the ground-state conformation is one in which the two aryl rings within each diarylmethyl moiety are twisted in the same sense, i.e., in which *both moieties are helical*.<sup>2a,e</sup> It follows that conformations with TPE skeletal  $C_{2h}$ ,  $C_s$ , and  $C_1$  symmetry (by which we mean the symmetry of the unsubstituted tetraarylethane skeleton) may be excluded, and that we need consider only those possessing TPE skeletal  $C_2$  or  $C_i$  symmetry. If the helicities<sup>2a</sup> of the two moieties are the same, the skeleton belongs to  $C_2$ , whereas if the helicities are opposite, the skeleton has  $C_i$  symmetry. In the following sections, we provide the basis for a decision between these two alternatives.

**Empirical Force Field Calculations.** In order to discriminate among various possible ground-state structures and thus to provide a starting point on which to base our analysis of tetraarylethanes, we resorted to empirical force field calculations<sup>7</sup> on two selected tetraarylethanes, TPE and TXE, differing appreciably in steric congestion. The successful calculation of ground-state structures of related triaryl systems<sup>2h,k</sup> provided a basis for confidence that these calculations would yield accurate ground-state structures for tetraarylethanes such as TPE and TXE, in which bonding and nonbonding interactions are similar to those experienced by the triaryl systems.

The force field and program used in these calculations have been previously discussed.<sup>2h</sup> The force field is based on Allinger's,<sup>8</sup> with aromatic parameters from Boyd's force field<sup>9</sup> scaled to match Allinger's. The input structures were optimized

using the pattern search minimization technique, with an energy criterion for minimization of  $10^{-2}$  kcal over one iteration. Since the torsional potential is usually extremely shallow, the torsional angle of the phenyl rings was modified and the structure was then optimized again. This precaution should be taken particularly with nonquadratic energy minimization procedures such as pattern search.<sup>10</sup> The full relaxation technique was used and the structure was optimized without any symmetry constraints.

In order to explore the possibility of torsional isomerism about the central ethane bond, we calculated strain energies for several gauche and anti conformers of TPE. Anti conformers with  $C_2$ ,  $C_i$ , and  $C_{2h}$  symmetry ( $|\phi| = 45^\circ$ , regular hexagonal phenyl rings) were considered as input structures. All of these minimized to the same  $C_2$  structure, or were allowed to minimize to a point from which it was obvious that the final structure would be  $C_2$ . No other conformers with anti methine hydrogens could be located on the potential surface. Gauche conformers with two helical diarylmethyl moieties (input  $|\phi| = 45^\circ$ ) were also considered. Three diastereomeric gauche rotamers are possible, two with the same helicity of the diarylmethyl moieties ( $C_2$ ) and one with opposite helicities. Of the three gauche rotamers, the most stable (least strained) had  $C_2$  symmetry and was more strained than the anti rotamer by 4.9 kcal/mol. Thus, the strain calculations indicate an anti  $C_2$  ground state for TPE, and less than 0.1% population of the gauche rotamers at equilibrium.

The ground state of TXE in an anti conformation was similarly calculated. Here again, only one conformer, with  $C_2$  symmetry, was located on the potential surface, regardless of the symmetry of the input structure.

Both TXE and TPE adopt an almost perfect anti  $C_2$  propeller conformation.<sup>11</sup> The  $\text{H-C}_{\text{ethane}}\text{-C}_{\text{ethane}}\text{-H}$  dihedral angles are  $179.4$  and  $176.4^\circ$ , respectively. There are two distinct sets of aryl rings in each molecule. Each set contains two rings which are situated on the same side of the idealized  $\text{H-C}_{\text{ethane}}\text{-C}_{\text{ethane}}\text{-H}$  plane, i.e., which bear a gauche relationship, and which are related by  $C_2$  symmetry (the  $C_2$  axis bisects the central bond and is perpendicular to the  $\text{H-C}_{\text{ethane}}\text{-C}_{\text{ethane}}\text{-H}$  plane). The agreement in dihedral angles between symmetry equivalent aryl rings is satisfactory, both for TPE ( $-5.1$  and  $-7.2^\circ$ ;  $-35.2$  and  $-36.7^\circ$ ) and for TXE ( $-23.6$  and  $-23.0^\circ$ ;  $-45.5$  and  $-45.7^\circ$ ). We emphasize that geminal rings in TPE and TXE are *not* symmetry equivalent, and there is therefore no reason to expect that the dihedral angles of such rings (i.e.,  $\text{H1-C1-C2-C3}$  and  $\text{H1-C1-C8-C9}$ ) are similar, let alone equal, in magnitude.

A comparison of corresponding bond lengths and angles in TPE and TXE reveals that the latter is a molecule under considerable strain, due to the large nonbonded interactions of the bulky 2,6-xylyl groups. Thus, the central ( $\text{C1-C1}'$ ) bond in TXE is stretched to  $1.574 \text{ \AA}$ , as compared to  $1.556 \text{ \AA}$  in TPE, the mean  $\text{C}_{\text{ethane}}\text{-C}_{\text{aryl}}$  bond length ( $\text{C1-C2}$  and  $\text{C1-C8}$ ) in TXE is  $1.554 \text{ \AA}$ , as compared to  $1.533 \text{ \AA}$  in TPE, and the

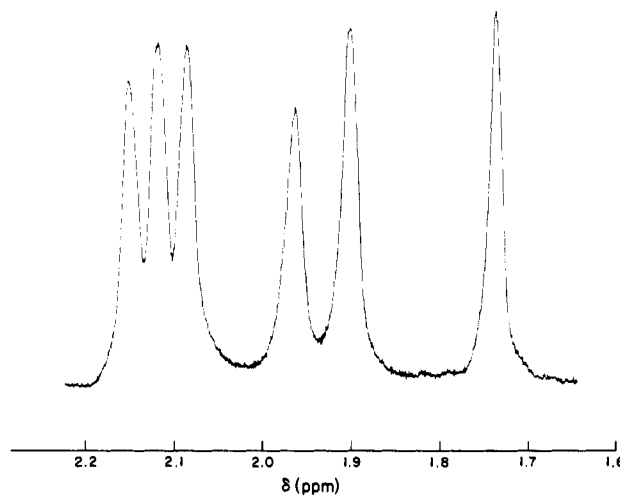
mean central C-C-C bond angle (C1'-C1-C2, C2-C1-C8, and C1'-C1-C8) in TXE is  $118.3^\circ$ , as compared to  $114.1^\circ$  in TPE. Our calculations reveal that eight nonbonded  $C_{\text{methyl}}-C_{\text{aryl}}$  distances in TXE are significantly shorter than the distance parameter for this interaction<sup>2h</sup> ( $d^* = 3.45 \text{ \AA}$ ); it is the presence of these highly unfavorable interactions which is a major cause of the bond angle expansion and bond lengthening.

Values for TXE are comparable to those calculated<sup>2h</sup> for the similarly overcrowded trimesitylmethane ( $C_{\text{methane}}-C_{\text{mesityl}}$  bond length =  $1.550 \text{ \AA}$  and central C-C-C bond angle =  $117.7^\circ$ ), but previous experience with this force field<sup>2h,k</sup> has indicated that distortions around the central carbon atom in such compounds are generally overestimated; for example, for trimesitylmethane, a  $C_{\text{methane}}-C_{\text{mesityl}}$  bond length of  $1.539 \text{ \AA}$  and a central C-C-C bond angle of  $115.9^\circ$  has been found by x-ray diffraction.<sup>2k</sup> Consequently, we expect that the calculated distortions in TXE bond lengths and angles may also be somewhat overestimated. Nevertheless, they are all still abnormally large. In particular, the marked elongation of the central bond in TXE accounts for the observation<sup>3c</sup> that TXE and 1,1,2,2-tetraesitylethane (TME), which may be assumed to experience nearly the same steric congestion around the central carbon atoms C1 and C1', homolyze to diarylmethyl radicals at elevated temperatures. Our conclusions are also supported by a recent study<sup>12</sup> of the crystal structure of TME. Although determination of an accurate molecular structure was frustrated by the occurrence of disorder in the crystals, it was possible to show that the molecule has a staggered conformation with the methine hydrogens in an anti position, that the mesityl rings are all twisted in the same direction, and that eight nonbonded distances between ortho methyl and  $C_{\text{aryl}}$  atoms are shorter than  $3.2 \text{ \AA}$ . The gross features of the x-ray structure of TME are therefore in accord with our calculated structure for the closely related TXE.

It is also interesting to compare our results for TPE and TXE with the x-ray structure of 1,1,2,2-tetrakis(2-methoxyphenyl)ethane (**1**),<sup>13</sup> which possesses a crystallographic center of symmetry and whose conformation deviates only slightly from  $C_{2h}$  symmetry. The geminal as well as the anti aryl rings have nearly equal, but oppositely signed, dihedral angles. The methoxy groups attached to the aryl rings are proximal to the methine hydrogens and experience remarkably short intramolecular O-methine H contacts ( $2.31$  and  $2.37 \text{ \AA}$ ). Thus, the conformation found<sup>13</sup> for **1** is decidedly not of  $C_2$  symmetry, in marked contrast to the results of our calculations for TPE and TXE. It must be remembered, however, that the generalizations concerning molecular propellers, which were expressed in the preceding section of this paper, rest on a data base which deals in the main with systems in which the rings are balanced, in the sense described above. Accordingly, since **1** does not fit this description, it is perhaps not overly surprising that it does not assume the shape of a molecular propeller. We note, however, that the central C-C bond length in **1** is  $1.555 \text{ \AA}$ , which agrees nicely with that calculated for TPE ( $1.556 \text{ \AA}$ ).

In summary, our empirical force field calculations indicate that tetraarylethanes in which the two ortho substituents on each phenyl ring do not differ appreciably in steric size (and in the absence of significant electronic effects not considered by molecular mechanics calculations) assume a ground-state conformation in which the methine hydrogens are anti, and in which the aryl rings are all twisted in the same direction, so that the structure assumes the appearance of a four-bladed molecular propeller (TPE skeletal  $C_2$  symmetry) when viewed in a direction perpendicular to the central bond and to the  $C_2$  axis, as in Figure 2.

**NMR Analysis of TME.** In order to obtain some information on the preferred conformation adopted by tetraarylethanes in solution, the NMR spectrum of TME was investigated. For TME, which is a representative of the simplest stereochemical



**Figure 3.** Ambient temperature (ca.  $30^\circ\text{C}$ ) 100-MHz  $^1\text{H}$  NMR spectrum (methyl region) of TME in  $\text{CDCl}_3$ .

class of tetraarylethanes, i.e., those in which all the aryl rings are the same and possess local  $C_2$  axes, the number of expected methyl resonances depends only on the molecular symmetry.

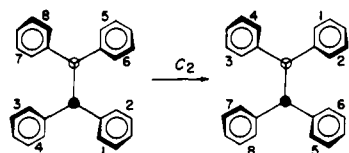
Although the NMR spectrum of TME was reported<sup>3c</sup> to feature "many absorptions of the protons of the aromatic methyl groups between 1.75 and 2.20 ppm, owing to hindered rotation of the phenyl rings", no further information was supplied. Figure 3 reveals that the methyl region of the  $^1\text{H}$  NMR spectrum of TME features six resonances of equal intensity. Four of these signals must arise from the ortho methyl groups and the other two from the para methyl groups. The finding that there are four symmetry nonequivalent ortho methyl groups rules out structures with  $C_{2h}$  and  $C_1$  symmetry which, in the absence of accidental isochrony, should give rise to two and eight ortho methyl signals, respectively, and is consistent only with  $C_s$ ,  $C_2$ , and  $C_i$  point group symmetry. Although a decision among these three alternatives for the ground state conformation of TME in solution is not possible on the basis of this NMR evidence,<sup>14</sup> it is clear from the results of our empirical force field calculations that (in the absence of significant solvation effects, which are not expected for TME) the molecular symmetry is  $C_2$ . Accordingly, an anti conformation with  $C_2$  symmetry may be safely assumed for the ground state of TME in solution, in harmony with the generalized conclusion stated in the preceding section.

#### Permutational Analysis and Isomer Table for Tetraarylethanes

Although the complete stereochemical analysis of a particular system can be worked out by a variety of procedures and by use of various algorithms, we have found<sup>2n,p,q</sup> that complex systems are most conveniently treated by application of simple group theoretical concepts. In our opinion, the analysis of chemical isomers and isomerizations in terms of permutations appears as the most satisfactory way of dealing with such systems.<sup>2n,p,q,15-17</sup> A case in point is the tetraarylethane system, for which an anti conformation with TPE skeletal  $C_2$  symmetry has been established (see above).

**The Permutation Group for Tetraarylethanes.** Consider a tetraarylethane in the TPE skeletal anti  $C_2$  conformation, in which the edges of the aryl rings are labeled with the numerals 1 through 8. An isomerization can be represented as a permutation of ligands (ortho and meta substituents) on these numbered sites. Thus, a  $C_2$  rotation corresponds to the permutation (15) (26) (37) (48).

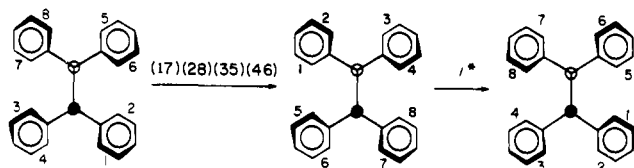
The group of permutations associated with the various ways of placing the four rings onto the ethane skeleton is the group



$S_4$ . This, however, includes certain permutations which do not correspond to stereoisomerizations. If one requires that the rings remain attached to their original central carbon atom, this group reduces to  $S_2[S_2]$ , where the first  $S_2$  corresponds to "end exchange" (i.e., the  $C_2$  point group rotation) and the second  $S_2$  to inversion of configuration at one central atom.

Since each aryl ring has two edges, a permutation can be associated with the interchange of these edges.<sup>24</sup> There are four aryl rings and thus four permutations, (12), (34), (56), and (78), generate the ring flip permutation group  $S_2 \times S_2 \times S_2 \times S_2 = (S_2)^4$ .

Combining the ring permutation group,  $S_2[S_2]$ , with the ring flip permutation group,  $(S_2)^4$ , results in the full permutation group of stereoisomerizations  $(S_2[S_2])[S_2] = R_{128}$  of order  $2^3 \cdot 2^4 = 128$ . The molecule has  $C_2$  skeletal symmetry and is therefore chiral. The enantiomer of each structure has the reversed helicity. Therefore, another operation, inversion of all coordinates ( $i^*$ ), must be included to account for this symmetry.<sup>18</sup> Reversal of helicity ( $h$ ) corresponds to the permutation (17)(28)(35)(46)\*, in which the asterisk designates the  $i^*$  operation. The full group of stereoisomerizations must therefore include the full permutation group considered above ( $R_{128}$ ) and its coset  $hR_{128}$  to give the full permutation-inversion group  $R_{128} \cup hR_{128} = R_{128} \times C_{i^*} = G_{256}$ .



The total number of stereoisomers ( $Z$ ) for a maximally labeled structure (all aryl rings different and all lacking a local  $C_2$  axis) can be found<sup>15</sup> using the formula (a simplified version of eq 1, below, where  $|B| = 1$ ):

$$Z = |G|/|A|$$

where  $G$  is the full permutation-inversion group and  $A$  is the rotational subgroup of the skeletal point group. Thus, for a maximally labeled tetraarylethane (TPE skeletal symmetry =  $C_2$ ), there are  $Z = |G_{256}|/|C_2| = 256/2 = 128$  isomers (32 with a given configuration at the central carbon atoms).

An alternative permutational representation<sup>24</sup> can also be useful in describing stereoisomerism in tetraarylethanes. Each ring has two differentiable edges. If we shade one edge and leave the other unshaded, the "ring flip" described above can be represented by the operation of edge interchange,  $e$ , under which the shadings are reversed. Since there are four rings, there are four such operations,  $e(1)$ ,  $e(2)$ ,  $e(3)$ , and  $e(4)$ . Let the operation  $h$  result in helicity reversal and the operations of  $c(1)$  and  $c(2)$  in change of configuration at each of the central ethane carbon atoms. (Since a  $C_2$  rotation is a proper rotation and will therefore lead to no new isomers, it need not be considered.) These seven elements ( $e(1)$ ,  $e(2)$ ,  $e(3)$ ,  $e(4)$ ,  $c(1)$ ,  $c(2)$ , and  $h$ ), each of order 2, can be used to generate a group  $H$  of order  $2^7 = 128$ . Each element in  $H$  corresponds to one of the 128 stereoisomers of a maximally labeled tetraarylethane.

Each of these seven generators is an involutory element, and each may therefore be abstractly associated with the binary numeral set {0, 1}. A set of seven two-valued descriptors results if we assign to each of the seven generators, in order, a value

**Table I.** Number of Isomers for Substituted Tetraarylethanes<sup>a</sup>

No. of identical rings	No. of rings with $C_2$ axes				
	0	1	2	3	4
0	128	64	32 <sup>f</sup>	16	8
2 <sup>b</sup>	128	64	32 <sup>g</sup>	16	8
2 <sup>c</sup>	64	32	16 <sup>f</sup>	8	4
3	64	32	—	8	4
2 + 2 <sup>d</sup>	32	—	8	—	2
2 + 2 <sup>e</sup>	72	—	20	—	6
4	20	—	—	—	2

<sup>a</sup> Based on TPE anti  $C_2$  skeletal symmetry (see text). <sup>b</sup> Systems with two chiral centers ( $abCHCHac$ ). <sup>c</sup> Systems with one chiral center ( $a_2CHCHbc$ ). <sup>d</sup> Systems with no chiral centers ( $a_2CHCHb_2$ ). <sup>e</sup> Systems with two constitutionally identical chiral centers ( $abCHCHab$ ). <sup>f</sup> Same whether the rings with  $C_2$  axes are attached to the same central carbon atom or not. <sup>g</sup> Same whether the rings with  $C_2$  axes are the same or not.

of either 0 or 1. The resulting ordered septuple uniquely defines each of the 128 stereoisomers of a maximally labeled tetraarylethane.

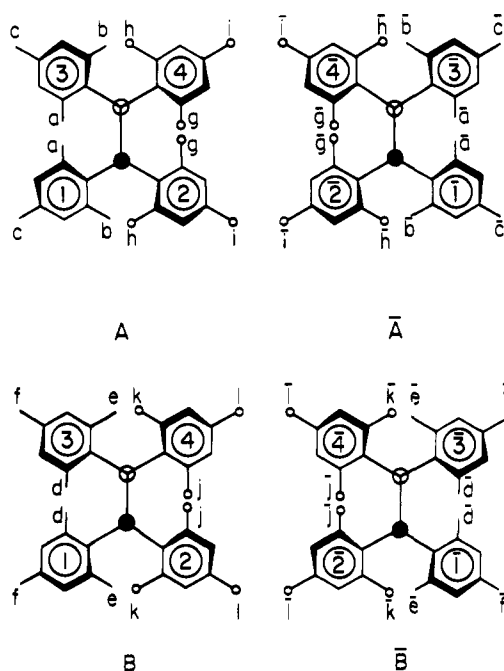
**Isomer Table.** To calculate the number of isomers ( $Z$ ) for any given substitution pattern, one can use the formula:<sup>15</sup>

$$Z = \frac{|G|}{|A||B|} \sum_{r=1}^k \frac{|A \cap C_r| |B \cap C_r|}{|C_r|} \quad (1)$$

where  $G$  is the full permutation-inversion group<sup>20</sup> ( $G_{256}$  for all configurations<sup>21</sup>),  $A$  is the rotational subgroup of the skeletal point group (TPE skeletal symmetry =  $C_2$ ),  $B$  is the subgroup of  $G$  containing permutations of nondifferentiable ligands (edges), and  $C_r$  is one of the  $k$  conjugacy classes of  $G$ .<sup>11</sup> The summed term in eq 1 will be nonzero only when  $C_r$  contains the identity or when  $B$  intersects with the conjugacy class containing the operation  $C_2$ . The number of isomers determined for each possible substitution pattern for  $C_2$  tetraarylethanes is given in Table I.

**Stereochemical Correspondence.** According to the principle of stereochemical correspondence,<sup>2e,f</sup> the analysis presented above for tetraarylethanes applies with equal force to tetraaryl systems in which the carbon atoms of the ethane joint are substituted by any element capable of existing in a tetrahedral arrangement, i.e., Si, Ge, P, As, etc. By using an algebraic description, the original concept of stereochemical correspondence has recently been expanded and generalized by Nourse,<sup>22</sup> who has shown that, for example, 1,1,2,2-tetraphenylethane and 1,5-hexadiene may be regarded as being stereochemically correspondent. Thus, although the isomerization processes in the two compounds differ vastly in their physical nature, i.e., ring flips vs. [1,3] and [3,3] shifts,<sup>22,23</sup> a relationship can nevertheless be established between these two apparently unrelated and chemically disparate systems.

According to this generalized concept, any system in which four twofold rotors are symmetrically attached to a two-atom skeleton capable of bearing six or four ligands can be regarded as stereochemically correspondent to tetraarylethanes. Two examples are  $Cl[(C_2H_5)_2N]_2WW[N(C_2H_5)_2]_2Cl$ <sup>24</sup> and tetraphenylethylene. For the latter compound,<sup>25</sup> as well as for tetramesitylethylene<sup>26</sup> and tetra-*p*-anisylethylene dication,<sup>27</sup> x-ray structure determinations have shown that these molecules adopt an idealized  $D_2$  ground state conformation in the solid state. <sup>1</sup>H NMR<sup>28</sup> and ESR<sup>29</sup> measurements are consistent with the same conformation in solution. For this system the full permutation-inversion group is the same ( $G_{256}$ ) as for tetraarylethanes. Thus,  $|G_{256}|/|D_2| = 256/4 = 64$  isomers (16 *dl* pairs with a  $Z$  configuration and 16 *dl* pairs with an  $E$  configuration) are expected for a maximally labeled tetraarylethylene.



**Figure 4.** The four conformational isomers (2 *dl* pairs) which correspond to racemic **2** in the TPE skeletal  $C_2$  conformation. Short lines on the rings denote methyl groups, and small circles denote methoxy groups. Barred letters and numerals denote enantiomeric relationships.

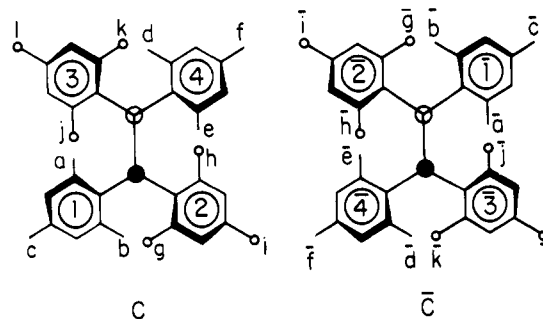
#### Static Stereochemistry of 1,2-Dimesityl-1,2-bis(2,4,6-trimethoxyphenyl)ethane

By virtue of the presence of *two* central carbon atoms, each of which has the potential of serving as a chiral center, suitably substituted tetraarylethanes are capable of exhibiting a stereochemical complexity which is denied to members of the previously studied classes of tri- and tetraarylmethane derivatives.<sup>2</sup> This complexity finds expression, for example, in the isomer table (Table I). In order to illustrate the intricacies connected with the combination of configurational and conformational isomerism in such systems, we turned to the study of a tetraarylethane possessing two constitutionally identical asymmetric carbon atoms, 1,2-dimesityl-1,2-bis(2,4,6-trimethoxyphenyl)ethane (**2**). On the assumption of TPE skeletal anti  $C_2$  symmetry, this molecule should exist in six stereoisomeric forms (Table I).

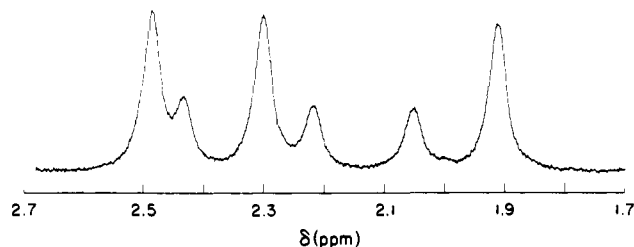
Compound **2** was obtained as a mixture of two isomeric products, melting points 249–250 and 258–262 °C, by reductive dimerization of racemic mesityl(2,4,6-trimethoxyphenyl)methanol. The mixture was separated by fractional crystallization (Experimental Section). Remembering that **2** has two constitutionally identical chiral centers, it is clear that the isomers are just the conventional diastereomers (i.e., the meso and racemic forms) expected for **2** on the time scale of rapid conformational interconversion. The question is: which is which? In the following section we show that an answer to this question is provided by the NMR spectra of the two isomers.

**Configurational Assignment to the Meso and Racemic Forms of 2 on the Basis of Their NMR Spectra.** There are six stereoisomers of **2**. Two diastereomeric *dl* pairs ( $A\bar{A}$  and  $B\bar{B}$  in Figure 4), with the same configuration at the two chiral centers (*A* and *B* are (*S,S*),  $\bar{A}$  and  $\bar{B}$  are (*R,R*)), correspond to racemic **2** on the time scale of rapid conformational interconversion, and one *dl* pair ( $C\bar{C}$ , Figure 5), with opposite configurations at the two chiral centers, corresponds to *meso-2* on the time scale of rapid conformational interconversion.

Examination of *C* (or  $\bar{C}$ ) reveals that this molecule is asymmetric, since the intersection of  $C_2$  (TPE skeletal sym-



**Figure 5.** The conformational *dl* pair which corresponds to *meso-2* in the TPE skeletal  $C_2$  conformation. See Figure 4 for additional comments.



**Figure 6.** Low-temperature (20 °C) 60-MHz  $^1\text{H}$  NMR spectrum (methyl region) of racemic **2** in chlorobenzene.

metry) and  $C_i$  (the skeletal symmetry of a *meso*  $abCHCHab$  system in the anti conformation) is  $C_1$ . Accordingly, none of the methyl or methoxy groups are symmetry equivalent to any of the others. It follows that the  $^1\text{H}$  NMR spectrum of *meso-2* in an achiral medium should feature six signals of equal intensity in the methyl region, and six signals of equal intensity in the methoxy region, under conditions where interconversion between the two conformational enantiomers (*C* and  $\bar{C}$ ) is slow on the NMR time scale, and in the absence of accidental isochronies.

In contradistinction, both diastereomers *A* (or  $\bar{A}$ ) and *B* (or  $\bar{B}$ ) have  $C_2$  point group symmetry, since the intersection of TPE skeletal symmetry ( $C_2$ ) and the skeletal symmetry of a *d* or *l*  $abCHCHab$  system ( $C_2$ ) is  $C_2$ . All atoms in *A*, as well as in *B*, are therefore related pairwise by symmetry. It follows that the  $^1\text{H}$  NMR spectrum of each diastereomer (*A* or *B*) should feature, in the absence of accidental isochronies, two signals for the ortho methyl (and methoxy) groups and one signal for the para methyl (and methoxy) groups, under conditions where interconversion between the conformational diastereomers ( $A \rightleftharpoons B$  and  $\bar{A} \rightleftharpoons \bar{B}$ ) is slow on the NMR time scale. If, as is to be expected, the population of the two diastereomers is not the same, the NMR spectrum of a mixture of *A* and *B* should therefore reveal, in the methyl as well as in the methoxy region, two *unequally* intense sets of signals, each consisting of three singlets of equal intensity, two for the ortho and one for the para groups.

The NMR spectrum of the lower melting isomer (mp 249–250 °C) at 20° in chlorobenzene (Figure 6) reveals six signals in the methyl region; four of these are due to the ortho and two to the para methyl groups. The three signals of higher intensity correspond to the methyl groups of the major diastereomer (arbitrarily associated with structure  $A\bar{A}$  of Figure 4), whereas the resonances of lesser intensity are due to the minor diastereomer ( $B\bar{B}$ ). At 20° the population ratio of  $A\bar{A}$  to  $B\bar{B}$  is 2.17:1 as determined from relative peak intensities. This corresponds to a free energy for the equilibrium  $A\bar{A} \rightleftharpoons B\bar{B}$  of  $\Delta G^\circ_{20} = 0.45$  kcal/mol (chlorobenzene). Although aromatic solvents resolved the methyl signals, they failed to

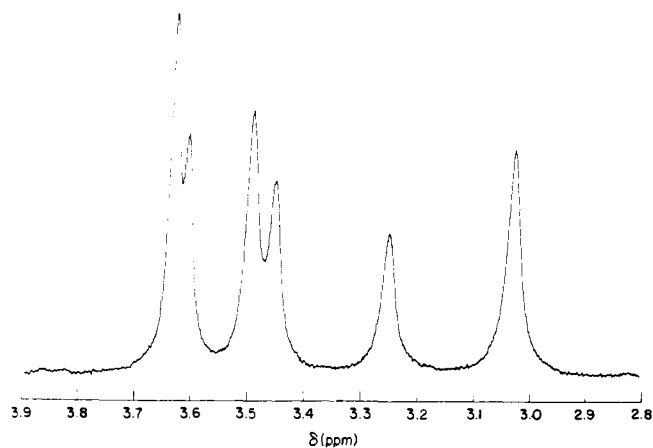


Figure 7. Low-temperature ( $-4\text{ }^{\circ}\text{C}$ ) 60-MHz  $^1\text{H}$  NMR spectrum (methoxy region) of racemic **2** in  $\text{CDCl}_3$ .

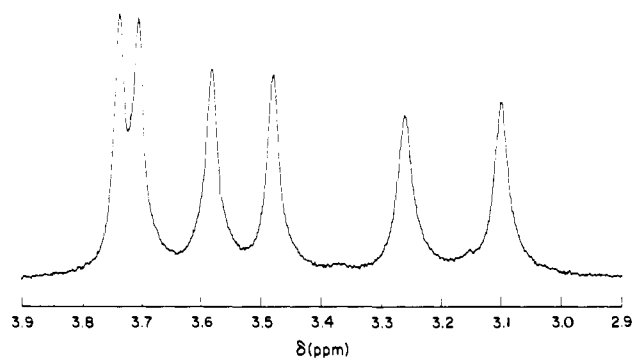


Figure 8. Low-temperature ( $-1\text{ }^{\circ}\text{C}$ ) 60-MHz  $^1\text{H}$  NMR spectrum (methoxy region) of *meso*-**2** in  $\text{CDCl}_3$ .

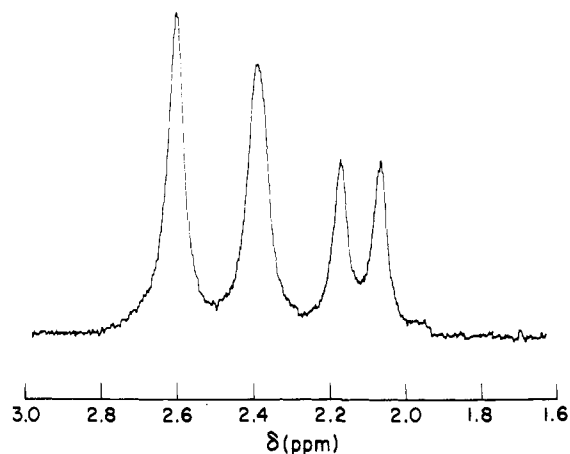


Figure 9. Low-temperature ( $-11\text{ }^{\circ}\text{C}$ ) 60-MHz  $^1\text{H}$  NMR spectrum (methyl region) of *meso*-**2** in  $\text{CDCl}_3$ .

remove accidental isochronies in the methoxy region. This problem was overcome by switching to chloroform solvent. The methoxy region of the  $^1\text{H}$  NMR spectrum of **2** (mp  $249\text{--}250\text{ }^{\circ}\text{C}$ ) in  $\text{CDCl}_3$  at  $-4\text{ }^{\circ}\text{C}$  is recorded in Figure 7. The expected six signals are clearly in evidence; the ratio of  $\text{A}\bar{\text{A}}$  to  $\text{B}\bar{\text{B}}$  is 1.37:1, corresponding to  $\Delta G^{\circ}_{-4} = 0.17\text{ kcal/mol}$  (chloroform).

A different NMR absorption pattern was found for the isomer with mp  $258\text{--}262\text{ }^{\circ}\text{C}$ . At  $-1\text{ }^{\circ}\text{C}$  in  $\text{CDCl}_3$ , the  $^1\text{H}$  NMR spectrum of this compound featured six equally intense signals in the methoxy region (Figure 8). However, in the methyl region the low temperature ( $-11\text{ }^{\circ}\text{C}$ )  $^1\text{H}$  NMR spectrum in chlorobenzene revealed four peaks in the intensity ratio 1:1:2:2 (Figure 9) instead of the six expected. We were unable

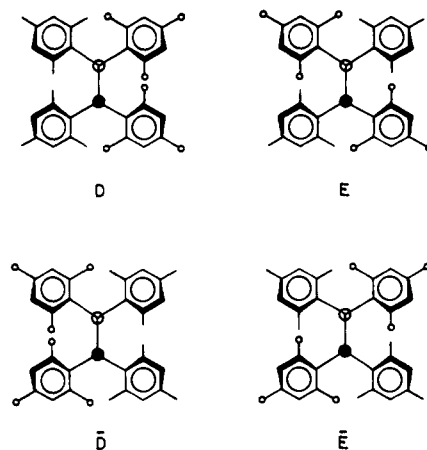


Figure 10. The possible stereostructures of **2** in a TPE skeletal  $C_s$  conformation. See Figure 4 for significance of small lines and circles.

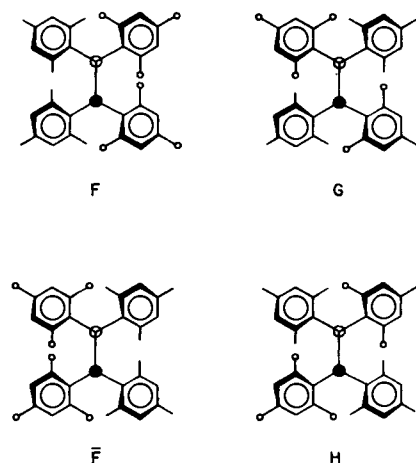


Figure 11. The possible stereostructures of **2** in a TPE skeletal  $C_i$  conformation. See Figure 4 for significance of small lines and circles.

to remove these accidental isochronies by changing the solvent or by further lowering the temperature.

The spectral evidence thus leaves no doubt that the lower melting isomer is a mixture of conformational diastereomers, i.e., that this isomer corresponds to racemic **2**, whereas the higher melting isomer consists of a single conformational *dl* pair and corresponds to *meso*-**2**.<sup>30</sup>

We previously remarked that while the NMR results for TME are consistent with  $C_2$  symmetry in the ground state, they cannot be used to rule out structures with  $C_s$  and  $C_i$  symmetry. The NMR results obtained for **2**, however, do allow some discrimination among the three alternatives.

Figure 10 depicts the structures of racemic and *meso*-**2** in which the TPE skeletal symmetry is  $C_s$ . The racemic form corresponds to a single conformational *dl* pair ( $\text{D}\bar{\text{D}}$ ), and the *meso* form to another ( $\text{E}\bar{\text{E}}$ ). All four stereostructures are asymmetric, since the intersection of TPE skeletal symmetry ( $C_s$ ) with *abCHCHab* skeletal symmetry ( $C_2$  for  $\text{D}$  and  $\bar{\text{D}}$ ;  $C_i$  for  $\text{E}$  and  $\bar{\text{E}}$ ) is  $C_1$ . It follows immediately that the  $^1\text{H}$  NMR spectrum of racemic, as well as of *meso*-**2**, should display six signals of equal intensity in the methyl and methoxy regions, contrary to observation. Consequently, TPE skeletal  $C_s$  symmetry is ruled out.

Figure 11 depicts the structures of racemic and *meso*-**2**, in which the TPE skeletal symmetry is  $C_i$ . The racemic form corresponds to a single conformational *dl* pair ( $\text{F}\bar{\text{F}}$ ), while for the *meso* form two achiral conformers ( $\text{G}$  and  $\text{H}$ ) are possible. Structures  $\text{F}$  and  $\bar{\text{F}}$  are asymmetric, since the intersection of

TPE skeletal symmetry ( $C_i$ ) with *abCHCHab* skeletal symmetry ( $C_2$ ) is  $C_1$ . However, in the case of G and H, the intersection of TPE skeletal symmetry ( $C_i$ ) with *abCHCHab* skeletal symmetry ( $C_i$ ) is  $C_i$ , and consequently all atoms in G and H are pairwise related by symmetry. Since G and H are diastereomers, one would therefore expect, under conditions of slow conformational interconversion ( $G \rightleftharpoons H$ ), that a mixture of G and H would exhibit precisely the same NMR characteristics (in an achiral solvent) as discussed for the mixture of diastereomers  $A\bar{A}$  and  $B\bar{B}$  (TPE skeletal  $C_2$  symmetry). It follows that if TPE skeletal  $C_i$  symmetry is adopted by **2**, it is now the racemic derivative which displays six signals of equal intensity in both the methyl and methoxy regions, while *meso-2* features two sets of three signals of unequal intensities in the methyl and methoxy region, i.e., the precise reverse of the situation described for TPE skeletal  $C_2$  symmetry. We note in this connection that no other substitution pattern of tetraarylethanes can lead to further discrimination between  $C_2$  and  $C_i$  skeletal point group symmetry on the basis of NMR characteristics alone (in an achiral medium). The only substitution patterns to consider are those in which some of the isomers have *molecular*  $C_2$  or  $C_i$  point group symmetry, i.e.,  $a_2CHCHa_2$  and racemic or *meso abCHCHab*. The former gives the same number and intensity of peaks for  $C_2$  and  $C_i$  skeletal symmetry since conformations having either symmetry can be assumed by the same molecule. The latter two distinguish  $C_2$  and  $C_i$  skeletal symmetry only if the configuration (racemic or *meso*) can be independently established (cf. discussion of **2** above).

### Experimental Section<sup>32</sup>

**1,1,2,2-Tetramesitylethane**, mp 230–231 °C dec, was prepared according to the literature.<sup>3c</sup> The <sup>1</sup>H NMR spectrum featured resonances at  $\delta_{CDCl_3}$  1.75 (3 H, s, CH<sub>3</sub>), 1.90 (3 H, s, CH<sub>3</sub>), 1.97 (3 H, s, CH<sub>3</sub>), 2.08 (3 H, s, CH<sub>3</sub>), 2.12 (3 H, s, CH<sub>3</sub>), 2.16 (3 H, s, CH<sub>3</sub>), 5.45 (1 H, s, CH), and 6.55 (4 H, m, aromatic H).

***dl*-Mesityl(2,4,6-trimethoxyphenyl)methanol**. A solution of 2-bromomesitylene (1.80 g, 90 mmol) in 100 ml of anhydrous ether was added dropwise with stirring to a 1000-ml flask containing magnesium turnings (2.16 g, 90 mmol) and 100 ml of ether. The reaction mixture was refluxed for 3 h. A solution of 17.6 g (90 mmol) of 2,4,6-trimethoxybenzaldehyde in 500 ml of ether was added dropwise to the refluxing solution. After 50 min, the mixture was poured onto crushed ice containing 5% HCl and the organic layer was diluted with chloroform, separated, and dried (MgSO<sub>4</sub>). The solvent was distilled at reduced pressure and the crude white solid obtained was recrystallized from ether to yield 15.6 g (55%) of white crystals, mp 113–115 °C. The <sup>1</sup>H NMR spectrum featured resonances at  $\delta_{CDCl_3}$  1.68 (1 H, br s, OH), 2.23 (3 H, s, CH<sub>3</sub>), 2.28 (6 H, s, CH<sub>3</sub>), 3.68 (6 H, s, OCH<sub>3</sub>), 3.77 (3 H, s, OCH<sub>3</sub>), 6.13 (2 H, s, aromatic H), 6.43 (1 H, br s, CH), and 6.77 (2 H, s, aromatic H).

Anal. Calcd for C<sub>19</sub>H<sub>24</sub>O<sub>4</sub>: C, 72.12; H, 7.65. Found: C, 71.92; H, 7.71.

***dl*- and *meso*-1,2-Dimesityl-1,2-bis(2,4,6-trimethoxyphenyl)ethane (2)**. A sample of mesityl(2,4,6-trimethoxyphenyl)methanol (20.0 g, 62 mmol) was suspended in 200 ml of acetone containing 100 ml of concentrated HCl (36%), and 20 g (166 mmol) of CrCl<sub>2</sub> (Alfa Inorganics) was added. The mixture was stirred at room temperature under a dry nitrogen atmosphere for 3 h. The suspension was filtered and the precipitate was washed several times with water. The crude product (17.0 g, 90% yield) was dissolved in hot benzene. On cooling, two fractions were collected: fraction I (6.0 g), mp 239–243 °C, and fraction II (6.0 g), mp 239–242 °C. Removal of the benzene from the mother liquors left fraction III (4.5 g), mp 227–232 °C. NMR analysis (see text) showed that fractions I and II consisted essentially of racemic **2**; no trace of *meso-2* was detected to within the limit of NMR sensitivity. Recrystallization of fractions I and II from benzene gave 10.5 g (55.5% yield) of pure *dl-2*, mp 249–250 °C dec. The <sup>1</sup>H NMR spectrum featured resonances at  $\delta_{CDCl_3}$  2.03 (3 H, s, CH<sub>3</sub>), 2.11 (3 H, s, CH<sub>3</sub>), 2.25 (3 H, s, CH<sub>3</sub>), 3.15 (3 H, br s, OCH<sub>3</sub>), 3.46 (3 H, br s, OCH<sub>3</sub>), 3.68 (3 H, s, OCH<sub>3</sub>), ca. 5.80 (2 H, br s, aromatic H), 5.92 (1, s, CH), and 6.50 (2 H, br s, aromatic H); mass spectrum *m/e* (rel intensity, %) 598 (M<sup>+</sup>, 1), 299 (100).

Anal. Calcd for C<sub>38</sub>H<sub>46</sub>O<sub>6</sub>: C, 76.22; H, 7.74. Found: C, 75.91; H, 7.62.

NMR analysis of fraction III revealed that it consisted of ca. 20% of the *meso* and 80% of the racemic isomer. The estimated total yield of *meso-2* is thus ca. 0.9 g (4.7%). Enrichment of the *meso* isomer was achieved by treatment of fraction III with hot acetone. On cooling, a crystalline product was obtained consisting of almost pure racemic **2**. The residue obtained upon evaporation of the mother liquors yielded a fraction which contained ca. 35% of *meso-2*. Additional crystallizations from acetone afforded 0.2 g of a product, mp 258–262 °C. NMR analysis (see text) indicated that this material was pure *meso-2*. The <sup>1</sup>H NMR spectrum showed resonances at  $\delta_{CDCl_3}$  2.10 (12 H, s, CH<sub>3</sub>), 2.28 (6 H, s, CH<sub>3</sub>), 3.07 (3 H, s, OCH<sub>3</sub>), 3.23 (3 H, s, OCH<sub>3</sub>), 3.37 (3 H, s, OCH<sub>3</sub>), 3.49 (3 H, s, OCH<sub>3</sub>), 3.68 (6 H, s, OCH<sub>3</sub>), 5.86 (6 H, br m, CH plus aromatic H), and 6.52 (4 H, br m, aromatic H); mass spectrum, base peak *m/e* 299 (no apparent M<sup>+</sup> peak).

Anal. Calcd for C<sub>38</sub>H<sub>46</sub>O<sub>6</sub>: C, 76.22; H, 7.74. Found: C, 76.00; H, 7.86.

**Notations and Conventions.** Permutations are written as (1625) and read: move whatever is in site 1 to site 6; move whatever is in site 6 to site 2, etc. |G<sub>n</sub>| means the order (number of elements) of the group G. G<sub>1</sub>[G<sub>2</sub>] is the wreath product of G<sub>1</sub> and G<sub>2</sub> or the composition of G<sub>1</sub> around G<sub>2</sub>. A "X" inserted between two group symbols means the direct product of the two groups. S<sub>n</sub> is the symbol for the symmetric group of *n* objects. C<sub>2h</sub>, C<sub>s</sub>, C<sub>i</sub>, C<sub>2</sub>, and C<sub>1</sub> are the usual point groups. C<sub>i</sub>\* is the group (of order 2) generated by *i*\*

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**Supplementary Material Available:** a table of the calculated structural parameters for TPE and TXE and a listing of the conjugacy classes for G<sub>256</sub> and G<sub>128</sub> (5 pages). Ordering information is given on any current masthead page.

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 (21) To calculate the number of isomers for a racemic or meso configuration of an  $abCHCHab$  skeleton separately, one uses for  $G$  the group  $G_{128} = (S_2 \times S_2) [S_2] \times C_2 = R_{64} \times C_2$ , which includes rigid rotations and inversion of both centers, but not inversion of a single center.<sup>11</sup>  
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 (30) This assignment is also consistent with the observation that meso 1,1,2,2-tetraarylethane derivatives generally have higher melting points than the corresponding racemic forms.<sup>8</sup>  
 (31) A decision between  $C_2$  and  $C_1$  skeletal symmetry could in principle be made by examining the NMR spectra in the presence of a chiral auxiliary reagent (solvent or shift reagent), since resonance doubling is possible for the diastereomeric mixture AA/BB ( $C_2$ ) but not for the diastereomeric mixture G/H ( $C_1$ ).  
 (32) Elemental analyses were performed by Professor G. Lo Vecchio at the University of Messina, Messina, Italy. Unless specified otherwise, NMR spectra were recorded on a Varian A-60D spectrometer at ambient temperature (ca. 40°C) and refer to ca. 20% solutions in  $CDCl_3$  containing tetramethylsilane ( $Me_4Si$ ) as internal reference. Mass spectra were obtained on an AEI MS-9 high-resolution mass spectrometer, with an ionizing voltage of 70 eV. All reactions which involved the use of organometallic compounds as reagents were carried out under a dry high-purity nitrogen atmosphere. Melting points were measured in a Thomas-Hoover Apparatus and are corrected.

## Stereochemical Analysis of 1,1,2,2-Tetraarylethanes. 2. Dynamic Stereochemistry of Selected Tetraarylethanes and the Use of Residual Stereoisomerism and Residual Stereotopism as a Tool for Differentiating among Divers Stereoisomerization Pathways

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**Abstract:** The dynamic stereochemistry of 1,1,2,2-tetraarylethanes is treated using a group theoretical approach. The possible rearrangement modes for such systems are given and the ring-flip mechanisms associated with these modes are discussed. The temperature-dependent <sup>1</sup>H NMR spectra of 1,1,2,2-tetramesitylethane (TME) and of racemic and meso 1,2-dimesityl-1,2-bis(2,4,6-trimethoxyphenyl)ethane (**1**) indicate that a variety of stereochemical exchange phenomena take place on the NMR time scale. The lowest energy pathway for stereoisomerization in these molecules is found to be the four-ring flip. Because of the occurrence of correlated rotation of the aryl rings, residual diastereotopism is observed in such compounds under the four-ring flip. At higher temperatures, the residual signals of **1** undergo coalescence by an exchange process, which corresponds either to a three- or a two-ring flip. A method has been designed based on group theoretical considerations, which permits discrimination among various possible rearrangement modes by a study of the residual stereoisomerism and/or residual diastereotopism exhibited by appropriately substituted derivatives of 1,1,2,2-tetraphenylethane.

In the preceding paper<sup>2</sup> (hereafter referred to as part 1) we investigated the static stereochemistry of 1,1,2,2-tetraarylethanes (hereafter simply referred to as tetraarylethanes). On the basis of empirical force field calculations and <sup>1</sup>H NMR spectroscopic measurements, we concluded that these systems adopt a ground-state propeller conformation, with anti methine hydrogens and TPE (tetraphenylethane) skeletal  $C_2$  symmetry, provided the two edges of each aryl ring do not differ appreciably in steric requirement. The racemic and meso forms of 1,2-dimesityl-1,2-bis(2,4,6-trimethoxyphenyl)ethane (**1**) were separated and the configurations of the two isomers were established on the basis of their <sup>1</sup>H NMR spectra. It was also observed that tetramesitylethane (TME) and **1** exhibit restricted rotation of the aryl rings on the NMR time scale. Consequently, variable-temperature NMR studies are of interest as a means of providing information on the sites exchanged by the stereoisomerization processes which such

systems are capable of undergoing, and on the energy requirements for these processes.

The present paper deals with the dynamic stereochemistry of TME and of **1**. We show how the use of a group theoretical approach is capable of providing the basis for a description of the possible rearrangement modes<sup>3</sup> in these systems, and for a facile interpretation of the great variety of stereochemical phenomena which can arise in more complex tetraarylethanes. In addition we demonstrate how this approach leads to a method involving the study of appropriately substituted derivatives of TPE, which can, in principle, be used to discriminate among the various possible rearrangement modes.

### Rearrangement Modes and Flip Mechanisms

In the investigation of the static and dynamic stereochemistry of tri- and tetraarylmethane derivatives, we found it convenient to analyze chemical isomers and isomerizations by