Conformations and Threshold Rotational Mechanisms of the (*Z*)-1,2-Diarylethene Moiety: A Structural Correlation Study

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The crystal structures of substituted (*Z*)-1,2-diarylethenes and (*Z*)-1,2-diarylcyclopropenes, -cyclobutenes, -cyclopentenes, and -cyclohexenes that were reported in the literature were retrieved from the Cambridge Structural Database, and the dihedral angles of the aryl rings with the double bond were plotted in a conformational map. Analysis of the data by the Structural Correlation method together with molecular mechanics calculations suggest that the conformation and the threshold rotational mechanism of the (*Z*)-1,2-diarylvinyl fragment strongly depend on its steric environment. In 1,2-diarylcyclopropenes the aryl rings are nearly coplanar with the double bond, whereas in 1,2-diarylcycloalkenes with larger rings a propeller conformation is adopted. The threshold rotational mechanism is the one-ring flip for (*Z*)-1,2-diphenylethene and 1,2-diphenylcyclobutene, and is the two-ring flip for 1,2-diarylcyclopentene and 1,2-diarylcyclohexene. The calculated rotational barriers of the aryl rings in the threshold mechanism for all systems were very low (0.2−2.4 kcal mol^{-1}). The different conformations and rotational behaviors are dictated by an interplay of conjugation and steric effects.

Introduction

1,1-Diarylethenes adopt a propeller conformation in which the rings (the propeller blades) are twisted in the same sense.[1,2] This conformation is chiral, and the two enantiomers differ in the sense of twist of the rings, i.e., in their helicity. These vinyl propellers display correlated rotation of the rings which is commonly analyzed in terms of “flip” mechanisms.[3] In these mechanisms, which involve helicity reversal, the rings rotate in unison in a conrotatory or disrotatory fashion. A flipping ring passes through the normal to the double bond plane while a nonflipping ring rotates in the opposite direction and passes through the double bond plane. Depending on the number of rings that flip (two, one or none), the mechanism is called a two-, a one-, and a zero-ring flip, respectively. The zero- and two-ring flips involve conrotatory rings rotation, whereas the one-ring flip involves disrotatory rotation. NMR and computational studies have indicated that, depending on the substitution pattern of the double bond and the aryl rings, both the one-ring and the two-ring flips are feasible as the rotational mechanism of lowest activation energy (threshold mechanism) of crowded 1,1-diarylethenols.[4,5] Calculations and analysis of crystal data by the structural correlation (SC, see below) method[6,7] indicate that for the parent 1,1-diphenylethene the one-ring flip mechanism is of somewhat lower energy than the two-ring flip.[8,9a] Application of the SC method to benzophenones revealed that they enantiomerize exclusively via a one-ring flip mechanism.[9b] The rotational behaviors of 1,1-diarylethenes and benzophenones were ascribed to the higher Ar−C═O (as compared to Ar−C═C) conjugation energy, which stabilizes the transition state of the one-ring flip pathway where one ring is coplanar with the carbonyl.

In this paper, we describe a study of the conformation and threshold rotational pathways of the (*Z*)-1,2-diarylethene moiety in the acyclic (**1** and **2**) and cyclic (*Z*)-1,2-diarylalkenes **3**−**6** using calculations and the SC method.[10] The flip mechanisms of the moiety adopting a propeller conformation are displayed in Figure 1. The conformations of the parent compounds **1** and **3a**−**6a** were studied by Hohlneicher and co-workers by photoelectron spectroscopy, UV, calculations, and, for **4a** and

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[1] For reviews on molecular propellers, see: Mislow, K.; Gust, D.; Finocchiaro, P.; Boettcher, R. J. *Fortschr. Chem. Forschr.* **1974**, *47*, 1. Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26. Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* **1985**, *127*, 1. Willem, R.; Gielen, M.; Hoogzand, C.; Pepermans, H. *Adv. Dyn. Stereochem*; Gielen, M., Ed.; Academic Press: New York, 1985; Vol. 1, p 207.

[2] Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 477. For a review on vinyl propellers, see: Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1997**, *30*, 307.

[3] Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 1535.

[4] Biali, S. E.; Nugiel, D. A.; Rappoport, Z. *J. Am. Chem. Soc.* **1989**, *111*, 846. Frey, J.; Schottland, E.; Rappoport, Z.; Bravo-Zhivotovskii, D.; Nakash, M.; Botoshansky, M.; Kaftory, M.; Apeloig, Y. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2555. Correction: *J. Chem. Soc., Perkin Trans. 2* **1995**, 2377.

[5] For reviews on polyarylethenols, see: (a) Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1988**, *21*, 175. (b) Hart, H.; Rappoport, Z.; Biali, S. E. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, 1990; Chapter 8, p 481.

[6] Bürgi, H.-B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153.

[7] Schweizer, W. B. In *Structure Correlation;* Burgi, H.-B., Dunitz, J. D., Eds.; VCH: Weinheim, 1994; Vol. 1, pp 369−404.

[8] For early calculations on 1,1-diphenylethene, see: (a) Stegemeyer, H.; Rapp, W. *Ber. Bunsen-Ges. Phys. Chem.* **1971**, *76*, 1665. (b) Baraldi, I.; Gallinella, E.; Momicchioli, F. *J. Chim. Phys.* **1986**, *83*, 653.

[9] (a) Kaftory, M.; Nugiel, D. A.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1989**, *111*, 8181. (b) Rappoport, Z.; Biali, S. E.; Kaftory, M. *J. Am. Chem. Soc.* **1990**, *112*, 7742.

[10] Presented in part: Gur, E.; Biali, S. E.; Rappoport, Z.; Kaftory, M. 56th Annual Meeting of the Israel Chemical Society, Jerusalem, Feb 11−12, 1991; Abstract 98.

10.1021/jo9907540 CCC: $18.00

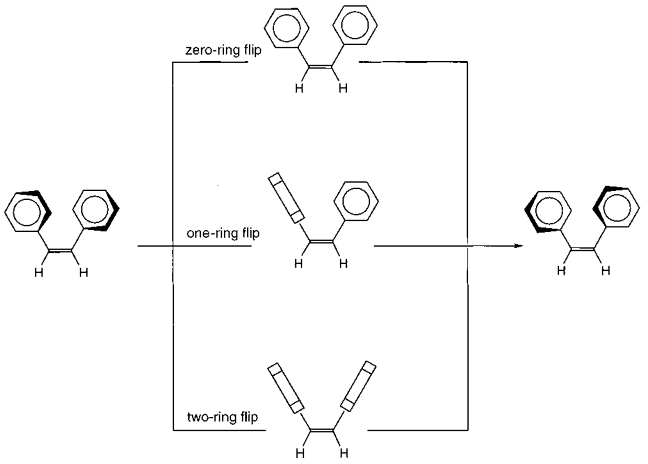
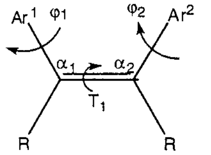
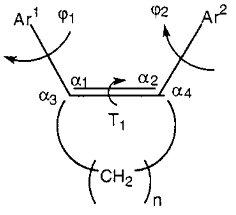


Figure 1. Idealized transition states of the zero-, one-, and two-ring flip processes as applied for (*Z*)-1,2-diphenylethene (**1a**). All processes result in enantiomerization of the propeller conformation. The hashed rectangle indicates an aryl ring perpendicular to the C(ipso)C=C plane.

6a, also by X-ray crystallography. These studies indicated that the dihedral angle φ_1 and φ_2 of the phenyl rings increase in the order **3a** < **4a** < **5a**< **6a**; diphenylcyclopropene **3a** possesses a nearly coplanar arrangement of the rings and the double bond.[11]

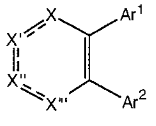


1 R = H
2 R = Me



3 n = 1
4 n = 2
5 n = 3

a Ar^1 = Ar^2 = Ph



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X, X', X'', X'''= various combinations of C,N,O,P,S
a X=X'=X''=X'''= CH$_2$, Ar^1 = Ar^2= Ph

Results

Conformational Map. The conformation and the rotational pathways of the (*Z*)-1,2-diphenylethene subunit can be characterized by the Ar−C=C dihedral angles φ_1 and φ_2. The conformational behavior can be conveniently analyzed by means of a conformation map[12] obtained by plotting the relative energy of the conformation vs the dihedral angles φ_1 and φ_2. The symmetry properties of the conformational map are related to the symmetry of the nonrigid molecular symmetry group of the molecule (isometric to C_{2v}).

The relative energies of the conformations of the parents (*Z*)-stilbene (**1a**), (*Z*)-1,2-diphenyl-2-butene (**2a**), 1,2-diphenylcyclobutene (**4a**), 1,2-diphenylcyclopentene (**5a**), and 1,2-diphenylcyclohexene (**6a**) were calculated using the dihedral driver option of the MM3(94) program,[13] changing φ_1 and φ_2 systematically by 10° steps.

Structural Correlation Method. The determination of the preferred conformation of a molecular fragment and its lowest energy rotational mode can in some cases be obtained by examination of many crystal structures possessing the fragment in different environments. As stated by Bürgi and Dunitz, "if a correlation can be found between two or more independent parameters describing the structure of a given molecular fragment in various environments, then the correlation function maps a minimum energy path in the corresponding parameter space".[6] The SC method can be applied to the 1,2-diarylethene fragment as follows: several crystal structures of compounds possessing the (*Z*)-1,2-diarylethene subunit and differing in the steric environments around the rings and in the packing arrangement in the crystal have been reported in the literature. These "perturbations" modify the dihedral angles of the subunit from their ideal values. When more than one rotational mode is possible, the change in dihedral angles should occur along the minimum energy rotational pathway. Provided that a sufficiently large number of X-ray structures possessing the fragment are available, it is expected that clustering of the data points will occur at the lower energy region of the conformational map, thus indicating the lowest energy conformation. Data points interconnecting clusters in the conformational map should trace the threshold rotational mechanism(s). The SC method is particularly suitable for low barrier rotational processes since as a result of the "flexibility" of the systems, small perturbations may significantly change the dihedral angles. The method can sometimes provide an "experimental" observation of the threshold mechanism in lieu of NMR data. This is particularly important for low barrier processes for which the slow exchange regime cannot be experimentally reached.

Data Retrieval. In the present study, all the available structures possessing the (*Z*)-1,2-diarylethene moiety were retrieved from the Cambridge Structural Database (updated June 1997), except that systems containing hetero aryl rings and organometallic compounds were excluded. In the majority of the retrieved structures the aryl rings were either unsubstituted or para-substituted. In addition to the acyclic (*Z*)-1,2-diarylethenes, 1,2-diarylcycloalkenes structures were retrieved and were divided into four groups: (i) 1,2-diarylcyclopropenes, (ii) 1,2-diarylcyclobutenes, (iii) 1,2-diarylcyclopentenes, and (iv) 1,2-diarylcyclohexenes. For these compounds the dihedral angles of the rings (φ_1 and φ_2), the Ar−C=C bond angles (α_1 and α_2), and the double bond twist angle (T_1) were analyzed. The dihedral angle of a given ring was defined as the angle between the C(ipso)C(α)=C(β) atoms and the mean plane of the ring carbons.

Conformations of (*Z*)-1,2-Diphenylethene and (*Z*)-2,3-Diphenyl-2-butene. Both electron diffraction[14] and calculations[15] indicate that (*Z*)-1,2-diphenylethene (**1a**) adopts a chiral propeller conformation.[16]

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[11] Hohlneicher, G.; Müller, M.; Demmer, M.; Lex, J.; Penn, J. H.; Gan, L.; Loesel, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 4483.

[12] For a discussion on conformational maps, see: Dunitz, J. D. *X-ray Analysis and the Structure of Organic Molecules*; Cornell University Press: Ithaca, NY, 1979; Chapter 10.

[13] Allinger, N. L. *Molecular Mechanics. Operating Instructions for the MM3 Program. 1989 Force Field (updated 5/6/92)*; Technical Utilization Corp.

[14] (a) Traetteberg, M.; Frantsen, W. B. *J. Mol. Struct.* **1975**, *26*, 69. (b) Fronczek, F. R.; Swan, A. M.; Corkern, J. A.; Gandour, R. D. *Acta Crystallogr., Sect. C* **1984**, *40*, 1875. (c) Andersonn, P. G. *Tetrahedron Lett.* **1994**, *35*, 2609.

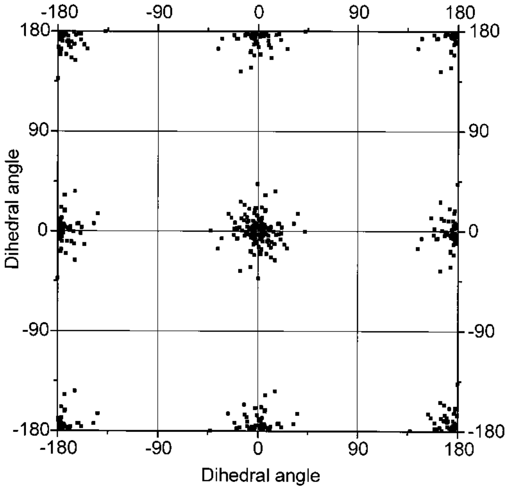


Figure 2. Conformational map of 1,2-diarylcyclopropenes **3**. Each point represents the crystallographically determined dihedral angles of the two rings of the diarylethene moiety. Concentration of the data points near the (0°,0°) region indicate a nearly planar preferred conformation of the fragment.

The conformational map of **1a** was calculated with the MM3 program. According to the calculations, **1a** adopts a propeller conformation of C_2 symmetry with Ph$-$C$=$C dihedral angles of 40°. These angles resemble those found by electron diffraction (43.2°).[14a] The calculated angles with the older MMP2 program were 38°.[11] The calculated energy barriers for the zero-ring, one-ring, and two-ring flip processes are 6.9, 2.4, and 2.9 kcal mol^{-1}; i.e., the one-ring flip is the threshold rotational mechanism. Since in the 1,2-diarylcycloalkenes the double bond is necessarily substituted by vicinal carbons, we calculated also the conformational map of 2,3-diphenyl-2-butene (**2a**) in order to assess the effect of the substitution on the conformation and rotational barriers. As shown by calculations, the double-bond substitution by two cis methyls does not modify the conformational preference for a propeller conformation; however, φ_1 and φ_2 increase from 40° in **1a** to 54° in **2a** in order to minimize the vicinal Ar/Me steric interactions. The calculated energies of the transition states of the zero-, one-, and two-ring flip processes (15.1, 6.3, and 0.2 kcal mol^{-1}, respectively) indicate that the threshold mechanism changes from that of **1a** and the two-ring flip is of lower energy than the one-ring flip pathway.

1,2-Diarylcyclopropenes. Thirty-eight data points possessing substructure **3** were retrieved. Examination of the crystal structures indicates that the bond angles α_1 and α_2 are in the 142°$-$157° range (mean: 151°) and are substantially larger than in the acyclic parent stilbene **1a**. The conformational map (Figure 2) indicates that the data points cluster radially at small dihedral angles (average: 3.4°) near the vicinity of the (0°, 0°) point. Hence, in contrast with **1a**, a nearly coplanar ArC$=$CAr arrangement represents the preferred conformation rather than a high-energy geometry. Previous calculations on the parent 1,2-diphenylcyclopropene with the QCFF/PI method indicated that the dihedral angles of the rings are 7°.[11] Interestingly, 18 (out of 38 data points)-"non-propeller" structures in which the two rings possess different sense of twist were retrieved. This is ascribed to the flatness of the energy surface near the minimum energy conformation.

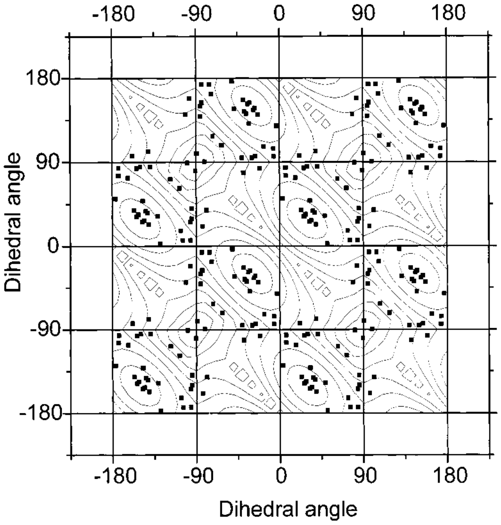
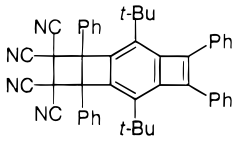


Figure 3. Conformational map of 1,2-diarylcyclobutenes **4**. The contours represent the calculated (MM3(94)) equipotential energy regions, with each contour representing an increase in energy of 1 kcal mol^{-1}.

1,2-Diarylcyclobutenes. MM3 calculations on the parent 1,2-diphenylcyclobutene **4a** indicate that the molecule adopts a propeller conformation of C_2 symmetry with Ar$-$C$=$C dihedral angles of 29°. MMP2 calculations[11] afforded a value of 24° for these angles, while in the crystal[11] these angles are 16° and 26°. According to the calculations, the transition states of the zero-, one-, and two-ring flips processes lie 4.4, 1.0, and 6.1 kcal mol^{-1}, respectively, above the propeller conformation.

Sixteen data points were retrieved for 1,2-diarylcyclobutenes. Since this data set is rather small, our conclusions are only tentative. Data points were observed near the calculated lowest-energy region (30°, 30°) and its symmetry equivalent regions in the potential energy map. In addition, data points were observed in the (0°,-90°/90°,0°) region and to a lesser degree in the (90°,90°) region, suggesting that both the one- and the two-ring flip pathways are feasible (Figure 3). This is in contrast to the MM3 calculations that predict a strong preference for the one-ring flip. However, examination of the structures corresponding to the data points in the (90°,90°) region indicate that severe in-plane steric interactions exist between the rings and bulky substituents (e.g., the *t*-Bu groups in **7**) that force the rings to adopt nearly perpendicular arrangements.



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(15) Sprague, J. T.; Tai, J. C.; Yuh, Y.; Allinger, N. L. *J. Comput. Chem.* **1987**, *8*, 581. Kao, J.; Allinger, N. L. *J. Am. Chem. Soc.* **1987**, *109*, 3817. Warshel, A.; Huler, E.; Rabinovich, B.; Shakked, Z. *J. Mol. Struct.* **1974**, *23*, 175. Huler, E.; Warshel, A. *Acta Crystallogr.* **1974**, *B30*, 1822. Warshel, A. *J. Chem. Phys.* **1975**, *62*, 214.

(16) In (*Z*)-*p*-ethinyl-*p*′-nitrostilbene (Hockless, B. C.; Whittall, I. R.; Humphrey, M. G. *Acta Crystallogr. C* **1996**, *52*, 3222) the dihedral angles are 51.5° and 12°. The remarkable small dihedral angle of the *p*-nitrophenyl ring (12°) is probably due to crystal packing forces, since AM1 calculations predict torsional angles of 44.4° and 40.9° for the *p*-ethinylphenyl and *p*-nitrophenyl rings, respectively.

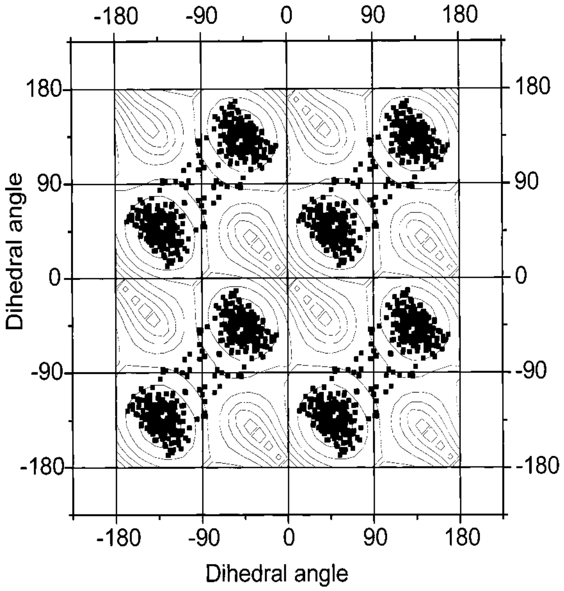
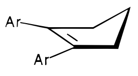


Figure 4. Conformational map of 1,2-diarylcyclopentenes **5**. Each contour represents an increase in steric energy of 1 kcal mol^{-1}.

1,2-Diarylcyclopentenes. MM3 calculations on 1,2-diphenylcyclopentene (**5a**) indicate that the molecule adopts a propeller conformation. However, in contrast to stilbene and 1,2-diphenylcyclobutene, the molecule does not adopt a conformation of C_2 symmetry but a conformation of C_1 symmetry in which the cyclopentene ring has an envelope conformation (**8**)[18] and the two rings are symmetry unequivalent (φ = 44.7° and 39.8°). Previous MMP2 calculations[11] reported dihedral angles of 38° while the X-ray crystallographically determined angles[18] are 48° and 44°.



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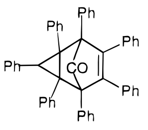

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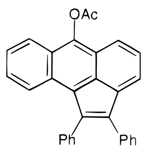

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The calculated energies for the zero-, one-, and two-ring flip are 8.4, 2.4, and 2.0 kcal mol^{-1}; the threshold rotational mechanism for 1,2-diarylcyclopentene is the two-ring flip.

The data set is the largest (108 data points) for 1,2-diarylethene moieties incorporated within a five-membered ring. Most points cluster near the "propeller" region (average dihedral angle: 50.4°). Notably, some structures (e.g., **9** and **10**) adopt a nonpropeller conformation where one of the rings is nearly perpendicular. This conformation is probably adopted in order to minimize the steric interactions of the rings with the substituent. Clusters representing enantiomeric conformations (e.g., (−50°,-50°) and (50°,50°)) are interconnected by data points located near the (90°, 90°) region, suggesting that the threshold rotation mechanism of the fragment is the two-ring flip (Figure 4), in agreement with the calculations.

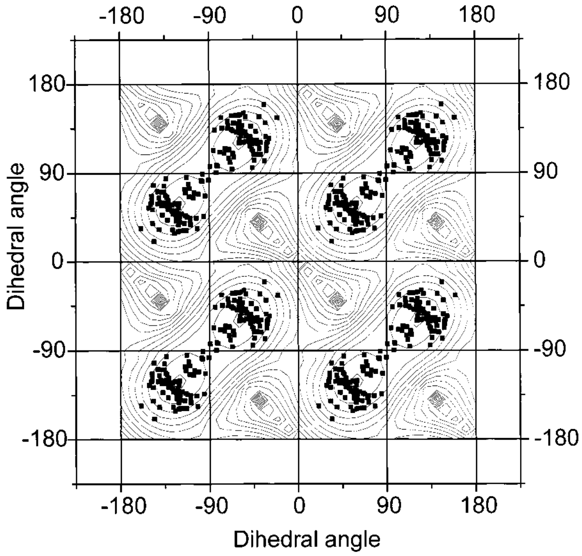
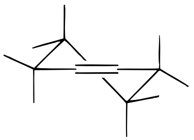


Figure 5. Conformational map of 1,2-diarylcyclohexenes **6**. Each contour represents an increase in steric energy of 1 kcal mol^{-1}.

1,2-Diarylvinyl Moieties Incorporated in Six-Membered Rings. Previous MMP2 calculations of **6a** yielded phenyl dihedral angles of 46°, while according to X-ray crystallography[11] these angles are 40° and 55°. The present MM3 calculations indicate that 1,2-diphenylcyclohexene adopts a propeller conformation of C_2 symmetry, with identical dihedral angles φ_1 and φ_2 of 51.4° and the cyclohexene adopts a half-chair conformation (**11**). The calculations indicate that the barrier for the two-ring flip (0.35 kcal mol^{-1}) is much lower than those for the zero- and one-ring flip (13.0 and 6.8 kcal mol^{-1}, respectively).



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Thirty-seven structures were retrieved in which the (*Z*)-1,2-diarylethene moiety is part of a six-membered ring (cf. **6**). They were subdivided into two groups: (i) 1,2-diarylcyclohexenes (i.e., with a single double bond) and (ii) structures in which the atoms X, X′, X″, and X‴ are carbons or heteroatoms.

In both cases, the data points concentrate near the (60°,60°) region (average dihedral angle: 60.4°) suggesting a preferred propeller conformation. In group i, the cyclohexene ring adopts a half-chair conformation. As observed for **5**, data points located near the (90°, 90°) region connect the clusters representing enantiomeric conformations (Figure 5). This suggests that the threshold mechanism is the two-ring flip, as suggested by the calculations. We note that the scatter of points from the (0°,0°) (90°,90°) diagonal is lower than for the (*Z*)-1,2-diarylcyclopentenes in Figure 4. No structure possessing a nonpropeller conformation was retrieved, but in **12** and **13** the dihedral angles of the rings are near the (90°,90°) region. These structures suffer from severe in-plane steric interactions forcing the rings to adopt near perpendicular orientations.

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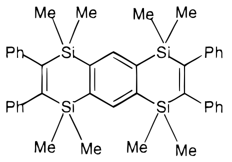
(17) The conformation of saturated five-membered rings is usually discussed in terms of the envelope and half-chair conformation (Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; p 758).

(18) Bernstein, J. *Acta Crystallogr., Sect. B* **1975**, *B31*, 418.



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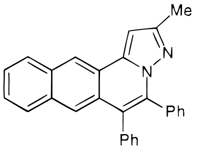

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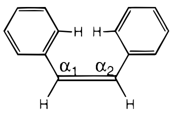
Discussion

Conformation of the (*Z*)-1,2-Diphenylethene Fragment. The conformation of the (*Z*)-1,2-diphenylethene fragment strongly depends on its steric environment. As shown previously by Hohlneicher et al.[11] and confirmed by the present calculations and crystal data, the dihedral angles of the rings become smaller as the cycloalkene ring size decreases, until aryl rings become nearly coplanar with the double bond in the cyclopropene derivatives. This is rationalized by the increase in the bond angles (α_1 and α_2) due to reduction of the endocyclic bond angles on decreasing the ring size. The larger the α angles, the larger the distance between the rings and hence the lower the mutual steric interactions between a pair of ortho hydrogens in vicinal rings in the coplanar arrangement with the double bond (cf. **14**). An additional structural factor that facilitates the nearly coplanar arrangement of the rings in the cyclic systems are the large exocyclic angles (α_3 and α_4). Their increase "removes" the methylene attached to the double bond from the vicinity of the rings, thus reducing their mutual steric interactions.

In all the other systems examined the propeller conformation was favored as a result of a compromise between energy reducing conjugation effects (maximal when the rings are coplanar with the double bond) and energy increasing repulsive steric effects (minimal when the rings are perpendicular to the double bond).



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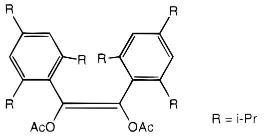

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Rotational Barriers and Threshold Rotational Mechanisms. The threshold rotational mechanism is different for **4** (one-ring flip) and **5**−**6** (two-ring flip). In all the cases examined, the calculated rotational barriers of the aryl rings in the threshold mechanism were low (0.2−2.4 kcal mol^{-1}), well below the range accessible by dynamic NMR experiments. Indeed, NMR data on the rotational barrier of such systems are scarce and have been reported only for crowded derivatives (e.g., for the ethenediol diacetate **15**).[19]

According to the MM3 calculations, the phenyl dihedral angles, the threshold rotational mechanism, and the calculated rotational barriers for the different flip mechanisms are similar for **2a** and **6a**. Since the bond angles α_1 and α_2 and the steric interactions between the aromatic rings and the methyl (or methylene) groups attached to the double bond are similar, it is reasonable that both the preferred conformation and the stereodynamics are similar.

Comparison of the calculated rotational barriers of **1a** and **2a** is instructive, since the barrier of zero-ring flip process is lower for **1a** (6.9 kcal mol^{-1}) than for **2a** (15.1 kcal mol^{-1}), while the opposite applies for the two-ring flip barrier (**1a**: 2.4, **2a**: 0.2 kcal mol^{-1}). Both phenomena can be partially or fully ascribed to an increase in the ground-state energy for the change **1a** → **2a** resulting from Ar/Me steric interactions that lead to larger dihedral angles φ. Whereas in **2a** the transition states energies for the zero-ring flip and one-ring flip processes increase as a result of the steric interactions between the coplanar ring(s) with the methyl groups, the transition-state energy of the two-ring flip is unaffected and the barrier for the process decreases.

The decrease in size of the cycloalkene ring facilitates attaining a coplanar arrangement of a ring with the double bond. This is reflected both in the preferred conformation of **3a**, in the calculated zero-ring flip barriers that diminish with the decrease in size of the cycloalkene ring (**6a**, 13.0; **5a**, 8.4; **4a**, 4.4 kcal mol^{-1}) and in the different threshold mechanisms of **4** (one-ring flip) and **5**−**6** (two-ring flip). In the conformation analogous to the zero-ring flip transition state of **3a**, the Ar/Ar steric interactions are small and the dominant stabilizing conjugation effects render it the preferred conformation. A similar situation is also suggested by the calculated rotational barriers of **4a**, in which the zero-ring flip barrier is lower than that for the two-ring flip. This is probably due to the same structural factors that favor the coplanar arrangement in **3a** (i.e., large exocyclic angles (α_1−α_4)), although these factors are present to a lesser extent than in cyclopropene **3** since the four-membered ring induces less severe distortions in the bond angles.

Attempted Structural Correlations. We searched for correlations between several structural parameters that may reflect the Ar/Ar interactions in the various systems. MM3 calculations indicate that the bond angles α_1 and α_2 for **5** and **6** increase in the transition state of the one-ring flip (e.g., from 121.5° in the ground state to 129.4° and 126.8° in the transition state of **6**), probably in order to alleviate the Ar/Ar steric interactions. As the "rotational coordinate" describing the progress along the one-ring flip pathway we chose the absolute difference in the dihedral angles $\Delta\varphi = |\varphi_1 - \varphi_2|$. Examination of the data indicates that α_1 and α_2 increase in a rough parallel to $\Delta\varphi$, but since this trend is only qualitative either when all the cycloalkene rings or a certain ring size are used, this approach was not investigated further.

Conclusions

Analysis by the Structural Correlation method of the crystal data of the (*Z*)-1,2-diphenylethene moiety incorporated into alicyclic systems indicates that both the preferred conformation and the threshold rotational mechanism depend on the size of the cycloalkene ring. In 1,2-diarylcyclopropenes, the two aryl rings are nearly coplanar with the double bond. 1,2-Diarylcyclobutenes, 1,2-diarylcyclopentenes, and 1,2-diarylcyclohexenes adopt a propeller conformation but differ in their threshold rotational mechanism (one-ring flip for **4**, two-ring flip for **5** and **6**).

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[19] (a) Faraggi, E. Z. MSc. Thesis, The Hebrew University of Jerusalem, 1992. (b) Faraggi, E. Z.; Frey, J.; Rappoport, Z. 11th IUPAC Conference on Physical Organic Chemistry, Ithaca College, Ithaca, Aug 2−7, 1992, Abstr. C-13.