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1,2-Diphenylcycloalkenes: Electronic and Geometric Structures in the Gas Phase, Solution, and Solid State

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Abstract: The geometric and electronic structures of several 1,2-diphenylcycloalkenes have been investigated by ultraviolet photoelectron spectroscopy (UPS), optical spectroscopy, X-ray crystal analysis, and theoretical calculations. The 1,2-diphenylcycloalkenes can be viewed as model *cis*-stilbenes in which cis–trans isomerization is not possible or at least is strongly hindered. In contrast to the unsubstituted cycloalkenes and the monophenylcycloalkenes, the first ionization potential of the diphenylcycloalkenes increases with increasing ring size. Optical spectra show an increasing blue shift of the first absorption band and an increasing Stokes shift with increasing ring size. These results have been compared to model calculations and to X-ray crystal structural data which allow us to establish connections between the changes in geometry and changes in the electronic structure of these systems. These results can only be explained by an increasing loss of planarity (decreasing conjugation) as the ring size increases in the 1,2-diphenylcycloalkene series.

I. Introduction

The cis–trans isomerization of stilbene represents one of the most studied, yet least understood photochemical reactions.[1] As part of a larger ongoing study into the photoreactions of model *cis*-stilbenes, we have noted profound differences in the photochemical reactions of a number of 1,2-diphenylcycloalkenes.[2] The differences in the photochemical reactivity seemed to be related to the size and the structure of the cycloalkene ring. However, the variations in reactivity could not simply be explained by the fact that the diphenylcycloalkenes with small rings no longer allow rapid deactivation of the electronically excited state by torsion of the central double bond. For example, the intramolecular photoreaction of 1,2-diphenylcyclopentene leading to its dihydrophenanthrene derivative is much faster than the corresponding reaction of 1,2-diphenylcyclobutene. 1,2-Diphenylcyclohexene, on the other hand, seems to be relatively photoinert, giving only an inefficient photoreaction to yield the dihydrophenanthrene. From our preliminary analysis of this reactivity pattern, we concluded that the initial geometries of these model *cis*-stilbenes may play a critical role in determining the nature of the initial excited state produced through Franck-Condon excitation as well as the subsequent photochemical reactions which occur from these initial excited states.

Previous detailed structural information on 1,2-diphenylcycloalkenes was only available for the five-membered-ring compound through an X-ray crystal structure of 1,2-diphenylcyclopentene.[3] Therefore, we have determined the X-ray crystal structures of 1,2-diphenylcyclobutene and 1,2-diphenylcyclohexene. While X-ray crystal structure determinations can give very specific structural information, one must always be aware that structures of molecules in the crystal may be considerably different than those in the gas phase or in solution. The differences between the solid state and the gas phase can be large, particularly for molecules like biphenyl or stilbenes. For example, *trans*-stilbene is found to be planar in the solid state,[4] but it is planar neither in the gas phase[5] nor in solution.[6-9]

Since our photochemical studies on 1,2-diphenylcycloalkenes were performed in solution,[2] we desired independent confirmation that the same structural features observed in the crystal structure determinations are present in the molecules as they exist in solution. This is a much more difficult problem, since indirect methods must be used for structural elucidation of molecules in solution. Therefore, we have utilized three independent methods to gain information on the molecular properties of these 1,2-diphenylcycloalkenes which may give insight into structures in solution or in the gas phase. These methods are ultraviolet photoelectron (UP) spectroscopy, electronic spectroscopy, and a variety of modern computational techniques (i.e., optimized force

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[1] Saltiel, J.; Ganapathy, S.; Werking, C. *J. Phys. Chem.* **1987**, *91*, 2755 and references contained therein.

[2] (a) Penn, J. H.; Gan, L.-X.; Eaton, T. A.; Chan, E. Y.; Lin, Z. *J. Org. Chem.* **1988**, *53*, 1519. (b) Penn, J. H.; Gan, L.-X., in preparation.

[3] Bernstein, J. *Acta Crystallogr., Sect. B* **1975**, *B31*, 418.

[4] Hoekstra, A.; Meertens, P.; Vos, A. *Acta Crystallogr., Sect. B.* **1975**, *B31*, 2813.

[5] Traetteberg, M.; Frantsen, E. B.; Mijlhoff, F. C.; Hoekstra, A. *J. Mol. Struct.* **1975**, *26*, 57.

[6] Dyck, R. H.; McClure, D. S. *J. Chem. Phys.* **1962**, *36*, 2326.

[7] Edelson, M.; Bree, A. *Chem. Phys. Lett.* **1976**, *41*, 562.

[8] Suzuki, H. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 379.

[9] Hohlneicher, G.; Dick, B. *J. Photochem.* **1984**, *27*, 215.

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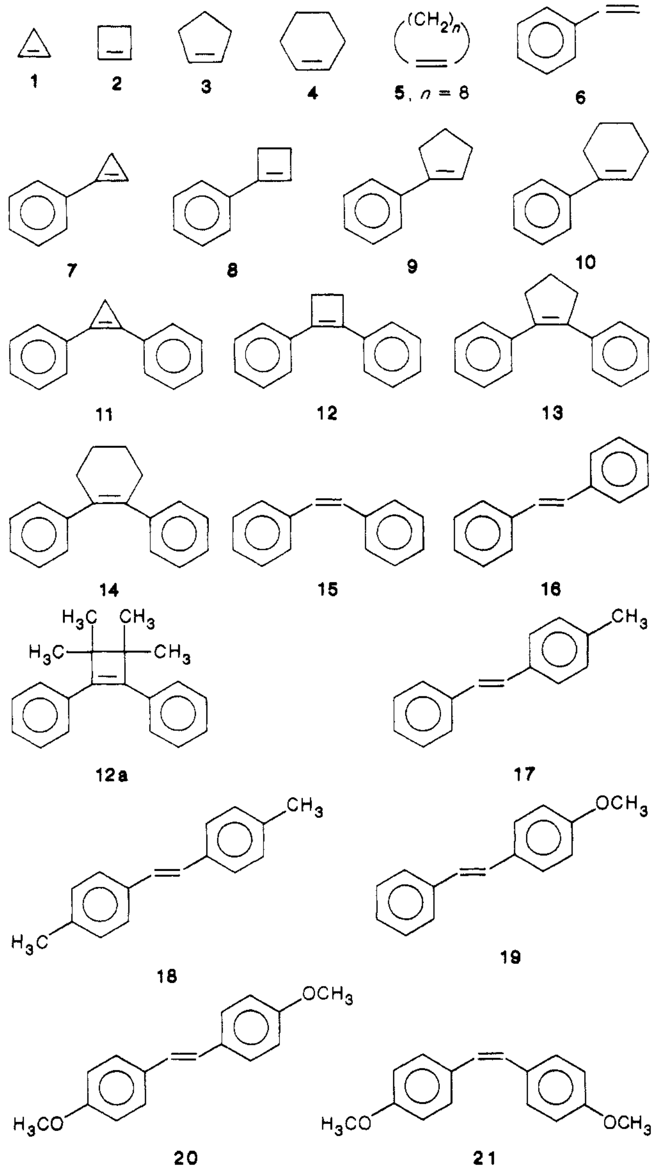
Chart I. Compounds Included in This Study



field calculations (MMP2[10] and QCFF/PI[11]) and semiempirical quantum chemical calculations (MNDOC[12])). The UP spectra and computational techniques relate to nearly free molecules (gas phase, ca. 10^{-4} Torr). Electronic spectra relate to molecules in dilute solution, the same medium in which our photochemical studies were performed.

Unfortunately, these spectral techniques do not provide direct information on the structure of the investigated compounds. In order to derive structural information, one has to rely on theoretical methods that relate changes in observable quantities (e.g., ionization potentials, excitation energies, transition probabilities) to changes in molecular structure. These theoretical methods are discussed in section III. Since any theoretical method is subject to a degree of uncertainty, we have shown how the method used for the interpretation of the UP spectra may be applicable to simpler compounds such as cycloalkenes, monophenylcycloalkenes, and *trans*- and *cis*-stilbenes. Having gained confidence in the application of this theory to the well-documented structure of simpler compounds, we can apply the technique to the UP spectra of diphenylcycloalkenes to gain gas-phase structural information about these compounds. Finally, we use electronic spectroscopy to confirm that the structural features deduced from the gas-phase measurements are applicable to the solution phase.

The numbering scheme for the compounds used in this study is shown in Chart I. Compounds **19** to **21** were included to clarify some uncertainties that exist in the literature and to make certain that the generally accepted assignment for unsubstituted *trans*- and *cis*-stilbene is indeed correct.

II. Experimental Details

Photoelectron spectra were measured at Cologne with a Leybold-Heraeus UP spectrometer (Model UPG200). The energy scale was calibrated with Ar (Ar $2p_{3/2}$ = 15.76 eV) and Xe (Xe $4p_{3/2}$ = 12.13 eV). Small amounts of Ar were added to each sample to monitor instrumental drift. All spectra were obtained with He I excitation ($h\nu$ = 21.2 eV).

UV–vis absorption spectra were measured at room temperture (RT) and at a temperature close to the temperature of liquid nitrogen (LNT). RT spectra were recorded on a Perkin-Elmer Model 555 UV–vis spectrophotometer. For the measurement of the low-temperature spectra, a homemade cryostat was used that fits into the UV spectrometer. In this cryostat, the holder for the sample cell is in direct contact with liquid nitrogen. The reference cell is kept at room temperature. The LNT spectra are not corrected for solute contraction. Emission, polarized emission, and polarized excitation spectra were measured with a homemade instrument described elsewhere.[13] All measurements were made in freshly distilled and dried 3-methylpentane (3-MP).

UP spectra were measured for compounds **10**, **12**, **12a**, **13–16**, and **19–21**. Electronic spectra were investigated for compounds **12**, **12a**, **13**, **14**, and **15**. Compounds **15**, **16**, **19**, and **20** were purchased from Aldrich and used directly. Other compounds investigated in this study were prepared by the authors from West Virginia University.[2]

Compound **21** was prepared by irradiation of the corresponding trans isomer and purified by silica gel column chromatography. GC analysis was used to ensure that the sample contained more than 99% of the cis isomer.

Crystal structure analysis was done for compounds **12** and **14**. Intensities were collected on an Enraf-Nonius CAD-4 diffractometer by a ω–2θ scan, using graphite monochromated Mo Kα radiation. Cell constants were determined from 25 accurately centered high-angle reflections, each measured at plus and minus 2θ. Two reflections were taken as standard reflections, and their mean change in intensity over the time of data collection was considered negligible. The structures were solved by direct methods with the E maps revealing positions for all non-hydrogen atoms. After isotropic refinement all hydrogen atoms were derived from difference electron density maps (except H(4A), H(4B), H(5A), H(5B) in **14**, because of the high thermal motion of C(4) and C(5)). They were treated isotropically in the final refinement.

All calculations were carried out with the Enraf-Nonius SDP system on a PDP 11/23 minicomputer. Tables of positional and thermal parameters have been included as supplementary material.

Crystal data for **12**: $C_{16}H_{14}$, M = 206.290. The crystal was found to be monoclinic, space group $P2_1$, with cell dimensions of a = 9.482 (2) Å, b = 6.714 (1) Å, c = 9.535 (2) Å, β = 100.05 (2)°, V = 597.63 Å^3, Z = 2, D(calcd) = 1.146 g cm^{-3}, μ(Mo Kα) = 0.601 cm^{-1}. After data reduction, 1093 reflections with $I > 2\sigma(I)$ were taken as observed ($\theta_{\max}$ = 27°). The final residuals are R = 0.037 and R_w = 0.039.

Crystal Data for **14**: $C_{18}H_{18}$, M 234.344, monoclinic, space group $P2_1/n$, with a = 18.604 (3) Å, b = 5.745 (1) Å, c = 13.487 (3) Å, β = 106.97 (2)°, V = 1378.83 Å^3, Z = 4, D(calcd) = 1.129 g cm^{-3}, μ(Mo Kα) = 0.590 cm^{-1}, 1187 observed reflections ($I > 2\sigma(I)$), R = 0.049, R_w = 0.055.

III. Calculations

An LCMO model was used to connect the experimentally observed ionization potentials with the geometry of the investigated systems. In this model, the molecular orbitals of a larger π system are described as linear combinations of molecular orbitals that are localized in subunits into which the larger system can be broken down. The energies for the π orbitals of the subunits can be obtained from the experimental UP spectra of the subunits by direct application of Koopmans' theorem.[14] In most cases, however, it is necessary to include a correction that takes into account the inductive effect of the group or the groups to which the given subunit is connected.

The LCMO model has been widely and successfully used for the interpretation of UP spectra. It has already been applied to

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(10) Sprague, J. T.; Tai, J. C.; Yuh, Y.; Allinger, N. L. *J. Comput. Chem.* **1987**, *8*, 581.

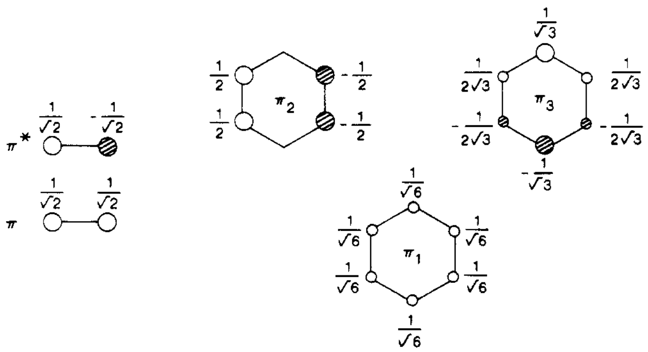
(11) Warshel, A.; Karplus, M. *J. Am. Chem. Soc.* **1972**, *94*, 5613.

(12) Thiel, W. *J. Am. Chem.* Soc. **1981**, *103*, 1413, 1420.

(13) Froelich, W. Dissertation, University of Cologne, 1979.

(14) Koopmans, T. *Physica* **1934**, *1*, 104.

Table I. Energies Used for the Localized Molecular Orbitals of the Subunits



subunit	VIP[a] (eV)	ϵ_{cor}[b] (eV)
ethylene		
π^*		−1.00
π	10.51	−10.26[c]
benzene		
π_3	9.25	−9.15[c]
π_2	9.25	−9.25[c]
π_1	12.20	−11.80[c]

[a] VIP, experimental vertical ionization potentials. [b] ϵ_{cor}, corrected orbital energies including inductive perturbations (see text). [c] From ref 15.

Table II. Experimental Ionization Potentials of Cycloalkenes and Related Compounds

			π	σ	
compd	ring size	ref	VIP (eV)	onset (eV)	first max (eV)
ethylene			10.51		
1	3	22	9.86	10.5	11.0
2	4	22	9.43	10.6	11.3
3	5	22, 24	9.1[a]	10.9	11.7
4	6	22, 24	9.03[a]	10.1	10.7
5	10	22	8.98	9.9	10.4
propene		23, 24	9.73		
trans-2-butene		23, 24	9.12		
trans-2-pentene		23, 24	9.04		

[a] Midpoint of the 0–0 and the 0–1 transition which have similar intensities in this compound.

Table III. Experimental and Calculated Vertical Ionization Potentials (in eV) for Styrene and Some Monophenylcycloalkenes

Experimental

compd	ring size	ref	π_4	π_3	π_2	σ onset	π_1
6		24	8.56[a]	9.25	10.53	11.5	12.1
8	4	15	8.22	9.25	10.06	10.9	12.1
9	5	15	8.15	9.22	9.86	11.9	12.1
10	6		8.29	9.12	9.74	10.7	12.0

Calculated

compd	ring size	θ (deg)	π_4	π_3	π_2	π_1
6		0	8.63	9.25	10.56	12.17
7	3	0	8.39	9.25	10.23	11.09
8	4	0	8.20	9.25	10.06	12.05
9	5	0	7.99	9.25	9.94	12.03
9	5	30	8.12	9.25	9.83	11.97
10	6	0	7.94	9.25	9.93	12.03
10	6	30	8.07	9.25	9.82	11.97
10	6	40	8.16	9.25	9.73	11.93

[a] Midpoint of the 0–0 and the 0–1 transition which have similar intensities in this compound.

monophenylcycloalkenes **8** and **9** by Bruckmann and Klessinger and we refer to their work[15] for further details. We deviate from the version given by these authors only insofar as we include the unoccupied antibonding π orbital of the double bond to derive a proper description of the π orbitals of stilbene-type systems that have a node at the central double bond. The energy of this orbital was arbitrarily set to −1.00 eV. The results of the calculations are virtually unchanged when this orbital energy is varied between 0 and −2 eV. The energies for the occupied π orbitals of the subunits were taken from the work of Bruckmann and Klessinger[15] (see Table I) as was the parameter for the interaction between two parallel carbon p_z orbitals at a distance of about 1.48 Å (β_0 = −2.45 eV). For nonplanar molecules where the two p_z orbitals at the ends of a twisted bond are no longer parallel, the interaction parameter is reduced by the cosine of the twist angle θ as shown in eq 1.

$$\beta(\theta) = \beta_0 \cos \theta \tag{1}$$

In order to study the influence of changes in geometry on the electronic spectra, we used CNDO/S calculations[16] because this method has been found to yield reliable results for larger nonplanar π systems. Two hundred energy selected singly and doubly excited configurations were included in the CI calculation (see ref 17 for details). The Pariser–Parr approximation[18] was used for the electron repulsion integrals. All other parameters were the same as in the final parametrization of the CNDO/S method.[19]

Molecular mechanics calculations were performed with both the MMP2[10] and the QCFF/PI method.[11] The results obtained with the two different methods are similar (compare Table VI). In most cases, the energy showed different local minima and a careful search was necessary to find the global one. The global minimum is usually very shallow with respect to asymmetrically twisted phenyl groups. For **12** for example, an energy of −3469.6 kcal/mol was found (QCFF/PI) for a structure in which both rings are twisted symmetrically by 22.5°. A structure in which one ring is twisted by 15.2° and the other by 31.7° yields an energy of −3469.3 kcal/mol. The shallowness of the calculated potential is in full accord with the very low frequencies observed for the torsional mode around the single bond: 17 cm^{-1} in tolane[20] and 18 cm^{-1} in *trans*-stilbene.[21] Due to the shallowness of the potential energy surface, the values for the twist angles given in Table VI have to be considered as the average of possibly unsymmetrical structures in which one ring is less twisted by ca. 10 to 15° and the other one twisted more strongly by approximately the same magnitude.

In addition to the molecular mechanics calculations, we also performed semiempirical quantum chemical calculations with the MNDOC method.[12] This method has been found to predict very reliable geometries for hydrocarbons with strained rings. The MNDOC program was obtained directly from Professor Thiel and used without further modification. The program allows us to include correlation effects by second-order Møller–Plesset perturbation theory. Bond lengths and bond angles within the phenyl groups were held constant during the geometry optimization. As we will show in detail (vide infra), the results of the MNDOC method are discouraging for the compounds studied here. The twist angle θ is undoubtedly overestimated in all cases.

The MMP2 calculations were done at West Virginia University and the LCMO, QCFF/PI, MNDOC, and CNDO/S calculations at the University of Cologne.

IV. Results and Discussion

Unsubstituted Cycloalkenes. The UP spectra of the unsubstituted cycloalkenes which were needed to estimate the input parameters for the LCMO calculations were measured by Bischof

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(15) Bruckmann, P.; Klessinger, M. *Chem. Ber.* **1978**, *107*, 1108.

(16) Del Bene, J.; Jaffe, H. H. *J. Chem. Phys.* **1968**, *48*, 1807, 4050; **1968**, *49*, 1221; **1969**, *50*, 1126.

(17) Dick, B.; Hohlneicher, G. *Theor. Chim. Acta* **1979**, *53*, 221.

(18) (a) Parr, R. G.; Pariser, R. *J. Chem. Phys.* **1953**, *21*, 446, 767. (b) Pariser, R. *J. Chem.* Phys. **1953**, *21*, 568.

(19) Ellis, R. L.; Kuehnlenz, G.; Jaffe, H. H. *Theor. Chim. Acta* **1972**, *26*, 131.

(20) Okuyama, K.; Hasegawa, T.; Ito, M.; Mikami, N. *J. Phys. Chem.* **1984**, *88*, 1711.

(21) Zwier, T. S.; Carrasquillo, M. E.; Levy, D. H. *J. Chem. Phys.* **1983**, *78*, 5493.

Figure 1. UP spectra of 1-phenylcyclohexene (**10**). See Table III for energies of band maxima.

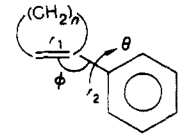
and Heilbronner[22] up to cyclodecaene (**5**). The relevant data from this publication are shown in Table II. The first vertical ionization potential (VIP) of the cycloalkenes decreases monotonically with increasing ring size. This can be explained by an increasing inductive effect with increasing size of the alicyclic part of the ring. Large rings behave similarly to 1,2-dialkylethylenes with larger alkyl substituents (compare Table II).

Gas-Phase Structures of Monophenylcycloalkenes. The VIPs for styrene (**6**) and three monophenylcycloalkenes (**8**, **9**, **10**) are listed in Table III. The UP spectrum of 1-phenylcyclohexene (**10**) which we were unable to find in the literature is shown in Figure 1. The VIPs obtained from this measurement are included in Table III. As mentioned in ref 15, the assignment of the lowest π orbital (π_1) is somewhat problematic in these compounds. π_1 is closely related to the lowest occupied π orbital of benzene which most investigators place at about −12.2 eV in Koopmans' approximation.[14] In benzene this assignment places the lowest π orbital below the highest occupied σ orbitals that give rise to the σ onset in the photoelectron spectrum of benzene. In styrene and in the monophenylcycloalkenes the band corresponding to π_1 is also most likely embedded in the first part of the σ region. Therefore, the determination of this VIP is somewhat uncertain.

Contrary to the unsubstituted cycloalkenes where we observed a monotonic decrease of the first VIP with increasing ring size, the first VIP now goes through a minimum which is reached for the five-membered-ring compound **9**. To find out if this minimum can be explained solely by differences in the inductive effect or if it is necessary to include geometrical effects, we followed the arguments of Bruckmann and Klessinger.[15] Using the input data shown in Table I, the application of the LCMO model to styrene **6** yields for the four π ionizations the energies shown in Table III. The calculated values are in excellent agreement with the experimental values. We therefore conclude that styrene is planar, or at least nearly planar, in the gas phase. Small deviations from planarity up to a twist angle θ of about 15° are not detectable from our experiments. The change of the π interaction at the twisted double bond is too small due to the slow variation of cos θ in the vicinity of $\theta = 0°$. The QCFF/PI calculation also predicts a planar structure for styrene (Table IV). However, because of the results that we found for *trans*-stilbene (vide infra), we do not put too much weight on the result of the force field calculation. On the other hand, MNDOC predicts a twist angle θ of 90° even after inclusion of the second-order Møller–Plesset correction. This result is definitely wrong since $\theta = 90°$ would lead to completely different ionization potentials and electronic spectra.

The π ionization for cyclobutene (**2**) is 9.43 eV (Table II). If we assume that the phenyl group has approximately the same inductive effect on the double bond of the cyclobutene ring as it has with respect to ethylene (−0.25 eV), we obtain an estimate of −9.20 eV for the orbital energy of the perturbed double bond. Together with the energies for the phenyl orbitals shown in Table I, this leads to the calculated ionization potentials for the four-membered-ring compound **8** shown in Table III. Again, the agreement with the experimentally observed data (Table III) is within the limit of experimental accuracy. The QCFF/PI force field also predicts **8** to be nearly planar (Table IV). The predicted angle between the double bond and the exocyclic single bond (133.8°) is almost identical with the angle found from the microwave structure analysis of cyclobutene (133.5°).[26]

Table IV. QCFF/PI Geometries for Styrene (**6**) and Several Monophenylcycloalkenes



compd n	6 0	8 2	9 3	10 4
θ (deg)	0	0.2	6.0	6.7
Φ (deg)	122.6	133.8	125.4	120.7
r_1 (Å)	1.34	1.35	1.34	1.36
r_2 (Å)	1.49	1.46	1.44	1.51
Φ' (deg)[e]	121.4[a]	133.5[b]	124.2[c]	119.5[d]

[a] Reference 25. [b] Reference 26. [c] Reference 27. [d] Reference 28. [e] Φ' is the experimental bond angle corresponding to Φ in the unsubstituted cycloalkenes.

By assuming planar structures, we obtained calculated VIP data for **7**, **9**, and **10** which are also shown in Table III. For each calculation the π ionization of the cycloalkene moiety was reduced by 0.25 eV to take into account the inductive effect of the phenyl group. For the three-membered-ring compound, this assumption is somewhat critical because of the different character of the exocyclic σ bond. Unfortunately, we cannot prove the predictions for **7** since we were unable to find any experimental data for this compound.

For the larger rings the model calculations predict a continuous decrease of the first ionization potential and an increasing energy difference between π_2 and π_4 (1.84 eV in **8** and 2.00 eV in **10**). This is not in accordance with the experimental observations. In addition to the minimum in the first VIP for the five-membered-ring compound mentioned above there is also a decrease in the π_2–π_4 separation (1.86 eV in **8**, 1.79 eV in **9**, and 1.44 eV in **10**). The only reasonable explanation for the observed deviations, especially for the decrease in the π_2–π_4 separation, is an increasing loss of conjugation between the double bond and the phenyl ring due to an increasing lack of planarity. For the five-membered-ring compound **9**, the best agreement with experimental data is reached for a twist angle of 30° (Table III). The QCFF/PI result (Table IV) predicts a much smaller twist angle of only 6°. Such a small twist angle could not explain why the first VIP of **9** is nearly the same as in **8** and especially not why the π_2–π_4 separation is smaller in **9** compared to **8**.

For the six-membered-ring compound **10**, a satisfying agreement is reached for a twist angle of the order of 40° to 50°. Only such a large twist angle can explain the strongly reduced π_2–π_4 separation that is observed for this compound. QCFF/PI again predicts a relatively planar structure (Table IV). Such a structure is not in accord with the observed behavior of the first ionization potential that reaches a minimum for **9** and then increases again for **10**. This structure is also not in accord with the further decrease of the π_2–π_4 separation observed for **10**.

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(22) Bischof, P.; Heilbronner, E. *Helv. Chim. Acta* **1970**, *53*, 1677.

(23) Mintas, M.; Jakopcic, K.; Klasinc, L. *Croat. Chem. Acta* **1983**, *56*, 263.

(24) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of He(I) Photoelectron Spectra of Fundamental Organic Molecules*; Halsted Press: New York, 1981.

(25) Carey, F. A. *Organic Chemistry*; McGraw Hill: New York, 1987.

(26) Bak, B.; Led, J. J.; Nygaard, L.; Rastrup-Andersen, J.; Sorensen, G. O. *J. Mol. Struct.* **1969**, *3*, 369.

(27) Rathjens, G. W. *J. Chem. Phys.* **1961**, *36*, 2401.

(28) Scharpen, L. H.; Wollrab, J. E.; Ames, D. P. *J. Chem. Phys.* **1968**, *49*, 2368.

Table V. Experimental Ionization Potentials for 1,2-Diphenylcycloalkenes (**11**–**14**), *cis*-Stilbene (**15**), *trans*-Stilbene (**16**), and Some Substituted Stilbenes (**17**–**21**)

compd	ref	π_7 (eV)	π_6 (eV)	π_5 (eV)	π_4 (eV)	π_3 (eV)	π_2 (eV)	π_1 (eV)	σ onset (eV)	σ max (eV)
11	37	7.49	9.03	9.03	9.38	10.00	(11.5–12.6)		11.0	11.2
						10.27				
12		7.71	8.96	9.11	9.36	9.95	(11.5–12.6)		10.25	10.5
12a		7.67	8.91	9.10	9.25	9.86			10.0	
13		7.77	8.83	9.10	9.57	9.90	(11.5–12.3)		10.5	11.3
14		7.87	8.83	9.07	9.45	9.60	(11.2–12.3)		10.0	11.4
15		8.20[a]	9.10	9.25	9.40	10.32	(11.5–12.3)		11.1	11.3
	32	8.17	8.99	9.22	9.36	10.27	11.8	12.0	11.0	11.3
	33	8.20	9.08		9.40	10.35			10.9	11.3
	37	8.10	8.97	8.97	9.20	10.30				
	38	7.90	8.82			10.07				
16		7.87[a]	9.06	9.06	9.33	10.41	11.7	12.0	10.9	11.3
	32	7.87	9.08	9.08	9.50	10.51	(11.7–12.2)		11.0	11.3
	33	8.00	9.25		9.55	10.60			11.0	11.4
	34	7.94	9.19	9.19		10.58	11.5		10.9	
	35	7.96	9.19	9.19	9.51	10.61	11.8	12.2	11.1	11.4
	23	7.79	9.06	9.06	9.37	10.48				
17	35	7.77	9.06	9.06	9.33	10.41	11.7	12.0	10.9	11.3
	36	7.63	9.02	9.02	9.33	10.33			10.9	11.1
18	36	7.54	8.82	8.82	9.00	10.12			10.7	11.0
19		7.59	9.08	9.08	8.88	10.14				
	35	7.57	8.86	9.15	9.15	10.21			10.8	11.2
20		7.15	8.99	8.99	8.37	9.68				
21		7.52	9.05	9.20	8.32	9.60			10.4	10.8

[a] This work.

From a comparison of the whole series of monophenylcycloalkenes it is obvious that increasing steric hindrance in the larger cycloalkene rings ($n > 2$) leads to twist angles that prevent an optimal π overlap between the phenyl group and the double bond. The QCFF/PI force field is not able to predict these changes properly. It seems to overestimate the stabilizing effect of π conjugation that favors more planar structures.

Gas-Phase Structures of Diphenylcycloalkenes: *trans*-Stilbene and Related Compounds. Considerable discussion exists in the literature concerning the degree of nonplanarity of the phenyl groups in *trans*-stilbene. It is well-known that the phenyl groups are nearly planar in the crystal,[4] but electron diffraction studies have shown that the phenyl groups are significantly twisted in the gas phase.[5] Since our ultimate goal was to infer a geometry for the diphenylcycloalkenes, we felt that it was necessary to verify that the LCMO model is applicable to stilbene-type molecules. The degree of planarity is expected to have a profound influence on the observed spectra of these systems.

Information relating to the structure of stilbene has been obtained by a variety of techniques. In the solid state, **16** is nearly planar.[4] In the gas phase, a twist angle of 32.2° has been reported based on the results of an electron diffraction study.[5] A force-field approach to a theoretical prediction based on MMP2[10] and QCFF/PI calculations predicts a nearly planar structure for the free molecule. In contrast to the force field calculations, all MNDO-type quantum chemical methods seem to strongly overestimate the twist angle. MNDOC predicts a structure in which the rings are symmetrically twisted by about 50°. Very large twist angles have already been found with MINDO/3 (90°)[29] and MNDO (shallow minimum between 60 and 90°).[30] Only the ab initio calculation of Wolf et al., the NDDO calculation of Hofmann and Birner, and the CS INDO calculation of Momicchioli yield a twist angle of 20°[31] in fair agreement with the electron diffraction results.[5]

The photoelectron spectrum of **16** was first interpreted assuming that the molecule is planar or at least nearly planar in the gas phase.[32-35] Recently the spectrum has been reanalyzed by Kobayashi et al.[36] These authors suggest that the spectrum is in much better agreement with the nonplanar structure deduced from electron diffraction studies than with a planar structure. The new analysis, however, presents new problems. The analysis is based in part on the ionization potentials of a *trans*-stilbene with fully twisted ($\theta = 90°$) phenyl rings. For this hypothetical structure, the ionization potentials of the inductively perturbed phenyl groups were estimated from ethylbenzene (8.78 and 9.27 eV) while the ionization potential of the inductively perturbed vinyl group was estimated from 2-butene (9.12 eV). However, Bruckmann and Klessinger[15] have shown that the inductive effect of a phenyl group on an ethylene π orbital is considerably smaller (−0.25 eV) than the inductive effect of a methyl group (−0.78 eV; compare data shown in Table II). Using the −0.25 eV for the inductive effect of a single phenyl group and assuming additivity, a value of 10.0 eV is obtained for the inductively perturbed π orbital of the double bond in **16**. Although this value is considerable higher than the value used in ref 36 we believe that this value represents a lower limit for the IP of the inductively perturbed double bond. The value is a lower limit because the inductive perturbation of different substituents is not strictly additive (note the IP data for ethylene, propene, and *trans*-2-butene shown in Table II). The value of 8.78 eV derived from ethylbenzene for the highest occupied π orbital of the inductively perturbed phenyl group (π_3) also differs considerably from the 9.15 eV obtained in ref 15. There is, however, an indication that the inductive effect on the phenyl groups is somewhat stronger in stilbene than in styrene. The band that corresponds to the two nearly unperturbed benzene orbitals (π_5 and π_6 in stilbene) is found at about 9.1 eV. In styrene, the corresponding band appears nearly at the same energy as in benzene itself (9.25 eV). Therefore, for stilbenes we use the following energies for the π orbitals of the phenyl groups as input parameters for the LCMO calculations: −9.05 eV (π_3), −9.15 (π_2),

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(29) Bally, T.; Haselbach, E.; Lanyiova, S.; Marschner, F.; Rossi, M. *Helv. Chim. Acta* **1976**, *59*, 86.

(30) Perrin, H.; Berges, G. *Theochem* **1981**, *1*, 299.

(31) (a) Wolf, A.; Schmidtke, H. H.; Knop, J. V. *Theor. Chim. Acta* **1978**, *48*, 37. (b) Hofmann, H. J.; Birner, P. *J. Mol. Struct.* **1977**, *39*, 145. (c) Momicchiolo, F.; Baraldi, I.; Bruni, M. C. *Chem. Phys.* **1983**, *82*, 229.

(32) Kobayashi, T.; Yokota, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 412.

(33) Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 196.

(34) (a) Hudson, B. S.; Ridyard, J. N. A.; Diamond, J. *J. Am. Chem. Soc.* **1976**, *98*, 1126. (b) Yip, K. L.; Lipari, N. O.; Duke, C. B.; Hudson, B. S.; Diamond, J. *J. Chem. Phys.* **1976**, *64*, 4020.

(35) McAlduff, E. J.; Chan, T. *Can. J. Chem.* **1978**, *56*, 2714.

(36) Kobayashi, T.; Suzuki, H.; Ogawa, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1734.

(37) Müller, C.; Schweig, A.; Vermeer, H. *J. Am. Chem. Soc.* **1978**, *100*, 8056.

(38) Kricka, L. J.; Lambert, M. C.; Ledwith, A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 52.

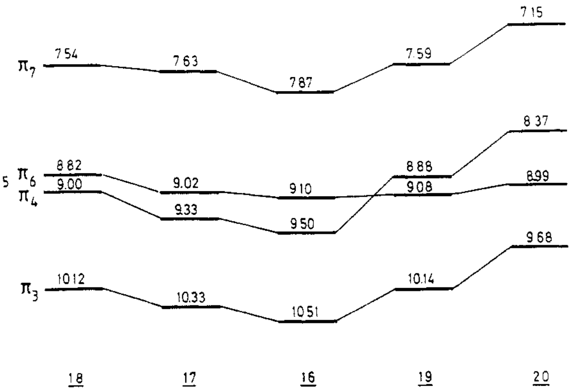


Figure 2. Energy level diagram for *trans*-stilbene (**16**) and several para-substituted *trans*-stilbenes.

and −11.80 (π_1). Together with the energy mentioned above of −10.0 eV for the π orbital of the vinyl group we obtained for *trans*-stilbene (all energies in eV)

	π_7	π_6, π_5	π_4	π_3	π_2	π_1
$\theta = 0$	7.94	9.15	9.28	10.54	11.90	12.37
$\theta = 30$	8.14	9.15	9.23	10.48	11.87	12.23
exptl av	7.9	9.1	9.5	10.6	(11.6 − 12.2)	

The values obtained for $\theta = 0°$ are in somewhat better agreement with the average (exptl av) of the experimental energies given by different authors (see Table V) than with those obtained for $\theta = 30°$. The differences are, however, not large enough to conclude that θ is definitely smaller than 30°, but we are also not able to confirm the conclusion of Kobayashi et al.[36] that the experimentally observed PE spectrum is in perfect agreement with the structure derived from the electron diffraction study.[5] There is still a possibility that the average twist angle in **16** is somewhat smaller than 32°. The problem with this structural assignment lies in the strong coupling between the twist angle θ and a possible twist (Ω) around the double bond. The 32° angle given for θ in ref 5 corresponds to $\Omega = 0°$. However, the data would allow a nearly equal fit to $\Omega = 10°$ and $\theta = 20°$. A further possibility is that the deviation from planarity arises from thermal motion in the very shallow torsional potential. Since **16** is one of the standards that will always be used to test computational methods with respect to their ability to predict proper twist angles, a refinement of the gas-phase structure in which special effort is put into narrowing the error limits for the twist angle is highly desirable.

To make certain that the assignment of the first four bands in the UP spectrum of *trans*-stilbene is correct, we investigated some para- and para, para'-substituted derivatives. The UP spectra of **17**, **18**, and **19** have already been measured,[35,36] but in all three compounds the bands corresponding to π_6, π_5, and π_4 overlap so strongly that an unambigous assignment of this part of the spectrum is hard to achieve. McAlduff and Chan,[35] for example, place π_4 in **19** around 9.10 eV and assign the band at 8.88 eV to π_6, assuming that π_5 and π_6 are no longer degenerate in this compound (compare Table V). To resolve these uncertainties, the UP spectra of **19** and **20** were measured. The results clearly show (Figure 2) that π_4 crosses π_5 and π_6 for strong +I substituents. For the methyl group the inductive perturbation is not large enough to cause this inversion. When we follow Kobayashi's assignment for **18**,[36] the shifts between unsubstituted *trans*-stilbene and its para, para'-substituted derivatives can be compared as follows

		π_7	π_4	π_3
$-CH_3$	abs	0.33	0.50	0.39
	rel	0.66	1.00	0.78
$-OCH_3$	abs	0.72	1.13	0.83
	rel	0.64	1.00	0.74
square of HMO coeff	abs	0.099	0.166	0.13
	rel	0.60	1.00	0.82

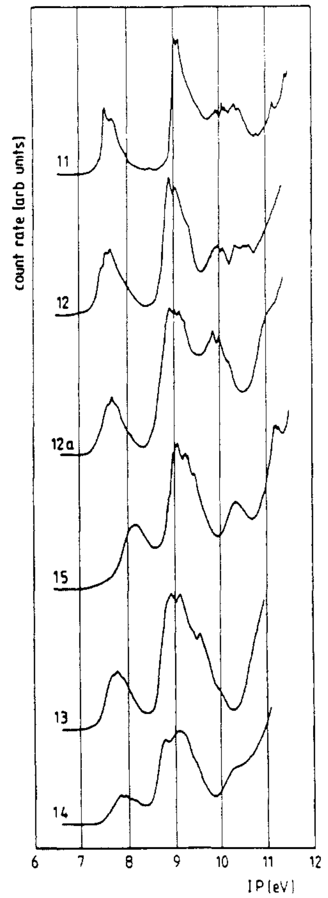


Figure 3. Low energy part of the UP spectrum of *cis*-stilbene (**15**) and several 1,2-diphenylcylcoalkenes.

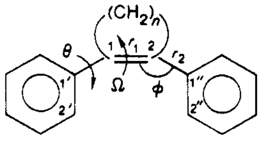
The excellent agreement between the relative shifts that are observed for the two substituents as well as the correspondnce with the extension of the corresponding orbital to the position of the substituent (as measured simply by the square of the HMO coefficient) puts a high probability on the assignment given in Figure 2. There is no doubt that π_4 is below π_5 and π_6 in unsubstituted *trans*-stilbene.

From the present analysis, it is also obvious that the independence of the energy difference between π_3 and π_7 from the nature of the para substituent is not a sufficient proof for the planarity of *trans*-stilbene and its para-substituted derivatives as suggested by McAlduff and Chan.[35] The experimentally observed independence only shows that the twist angle θ is approximately the same for different para substituents, an observation that is not surprising.

Gas-Phase Structures of Diphenylcycloalkenes: *cis*-Stilbene. The low-energy part of the UP spectra for *cis*-stilbene and several 1,2-diphenylcycloalkenes is shown in Figure 3 and the corresponding vertical ionization potential data are gathered in Table V. As in the case of *trans*-stilbene, VIPs given by different authors usually agree within one-tenth of an eV. Ionizations related to σ orbitals (mainly from C–H σ bonds) start around 10.5 to 11.0 eV in these compounds. Again the last two π ionizations (π_1 and π_2) are embedded in a range of σ bands. Therefore, their assignment, together with the attributed energies, is only tentative.

Contrary to what was observed for the unsubstituted cycloalkenes the first VIP increases with increasing ring size. On the basis of our analysis of the UP spectra of the monophenylcycloalkenes, this increase cannot be caused by changes in the inductive effect of the alicyclic part of the cycloalkene ring. The +I effect on the π system certainly increases with increasing ring size which should result in a decrease of the first VIP. To find out how far the observed increase is again related to changes in molecular geometry we first examine *cis*-stilbene since we have information on the gas-phase structure of this compound from the electron

Table VI. Experimental and Calculated Structural Data for *cis*-Stilbenes and Several 1,2-Diphenylcycloalkenes



		r_1 (Å)	r_2 (Å)	Φ (deg)	Ω (deg)	Θ (deg)	$d_{2'-2''}$	ref to other calcns
15	MMP2	1.35	1.48	126	9	38.0	3.1	10, 40, 41
n = 0	QCFF/PI	1.35	1.49	127	9	38.0	3.1	
	QCFF/PI	1.350	1.486	127.0	9	35		42
	exptl[a]	1.34	1.49	129.5		43.2	3.2	
11	MMP2							
n = 1	QCFF/PI	1.34	1.42	151	4	7	5.6	
	exptl							
12	MMP2	1.35	1.46	137	9	24	3.3	
n = 2	QCFF/PI	1.36	1.46	136	9	23	3.3	
	exptl	1.35	1.47	136.5	10.3	16/26	3.4	
13	MMP2	1.35	1.48	127	8	38	4.2	10, 40, 41
n = 3	QCFF/PI	1.36	1.49	128	10	36	4.2	
	exptl[b]	1.34	1.48	128.6	7.5	44/48	3.4	
14	MMP2	1.35	1.49	122	10	46	3.1	
n = 4	QCFF/PI	1.36	1.51	122	10	50	3.3	
	exptl	1.33	1.49	125	6.7	40/55	3.3	

[a] Reference 39 (electron diffraction). [b] Reference 3 (X-ray structure).

Table VII. Calculated Ionization Potentials (in eV) for *cis*-Stilbene and Several 1,2-Diphenylcycloalkenes for Different Twist Angles θ_1 and θ_2 and Different Values of the Through-Space Interaction between C Atoms 2′ and 2″ (β')[a]

compd	$\epsilon_=$	θ_1	θ_2	β'	π_7	π_6	π_5	π_4	π_3	π_2	π_1
15	−10.0	30	30	0	8.14	9.15	9.15	9.23	10.48	11.87	12.23
	−10.0	40	40	0	8.29	9.15	9.15	9.19	10.42	11.86	12.14
	−10.0	30	50	0	8.30	9.15	9.15	9.18	10.42	11.85	12.14
	−10.0	50	50	0	8.46	9.15	9.15	9.15	10.35	11.84	12.04
	−10.0	30	30	0.3	8.11	9.08	9.19	9.28	10.48	11.93	12.18
	−10.0	30	30	0.5	8.09	9.03	9.20	9.33	10.48	11.97	12.15
	−10.0	30	30	0.7	8.07	8.98	9.20	9.39	10.48	12.00	12.12
	−10.0	40	40	0.3	8.26	9.08	9.18	9.26	10.42	11.91	12.09
	−10.0	40	40	0.5	8.24	9.03	9.18	9.32	10.42	11.95	12.06
	−10.0	50	50	0.3	8.44	9.08	9.15	9.25	10.35	11.89	11.99
11	−9.31	0	0	0	7.64	9.15	9.15	9.28	10.28	11.90	12.24
12	−8.93	30	30	0	7.66	9.15	9.15	9.23	10.03	11.87	12.08
	−8.98	30	30	0.3	7.64	9.07	9.19	9.28	10.03	11.93	12.03
	−8.93	30	30	0.5	7.63	9.02	9.20	9.33	10.03	11.97	12.00
	−8.93	40	40	0.3	7.80	9.07	9.18	9.26	9.93	11.91	11.97
13	−8.60	45	45	0.7	7.68	8.97	9.16	9.37	9.75	11.85	11.98
14	−8.53	55	55	0.5	7.90	8.98	9.13	9.27	9.61	11.75	12.00

[a] $\epsilon_=$ orbital energy of the inductively perturbed double bond (in eV); θ_1, θ_2 twist angles (deg) β' interaction between C atoms 2′ and 2″ (in eV).

diffraction study of Traetteberg and Frantsen[39] (see Table VI). The twist angle found in this study is 43.2°, but again, the error limits are relatively large (±10°). The molecular mechanics calculations predict a somewhat smaller bond angle Φ than observed experimentally and also a somewhat smaller θ (Table VI). The overall agreement between calculated and observed geometry is, however, very good.

The results of a series of LCMO calculations are shown in Table VII. The same input parameters should apply to **15** that have been used for **16**. The only degrees of freedom that are available are the twist angles, θ_1 and θ_2, of the two phenyl groups. For a symmetric twist of 40° we find a π_3–π_7 separation that matches the experimental value nearly perfectly. However, the calculation leaves no explanation for the observed broadening in the π_4–π_6 region. Since the molecular mechanics calculations predict very shallow energy minima with respect to a slightly asymmetric twist of the phenyl groups, we also performed an LCMO calculation for such a structure (Table VII). The results clearly show that we cannot expect the UP spectra to discriminate between symmetrically and asymmetrically twisted phenyl groups. The result for the asymmetrically twisted phenyl groups is practically the

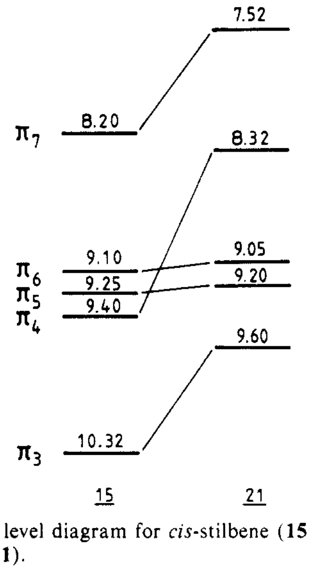


Figure 4. Energy level diagram for *cis*-stilbene (**15**) and *p,p*′-dimethoxy-*cis*-stilbene (**21**).

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(39) Traetteberg, M.; Frantsen, W. B. *J. Mol. Struct.* **1975**, *26*, 69.
(40) Kao, J.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 975.
(41) Kao, J. *J. Am. Chem. Soc.* **1987**, *109*, 3817.
(42) (a) Warshel, A.; Huler, E.; Rabinovich, B.; Shakked, Z. *J. Mol. Struct.* **1974**, *23*, 175. (b) Huler, E.; Warshel, A. *Acta Crystallogr.* **1974**, *B30*, 1822. (c) Warshel, A. *J. Chem. Phys.* **1975**, *62*, 214.

same as that for a symmetric twist with the same average angle.

To make sure that π_4 is still below π_5 and π_6 in **15**, we synthesized *p,p'*-dimethoxy-*cis*-stilbene, **21**, and measured its UP spectrum. The observed shifts (see also Figure 4) are somewhat smaller than in the case of **16**, but the relative shifts are in perfect agreement with the ones observed there. There is no doubt that π_4 is located below π_5 and π_6 in **15** as well as in **16**.

		π_7	π_4	π_3
$-OCH_3$	abs	0.67	1.08	0.72
	rel	0.62	1.00	0.67

Since asymmetrically twisted phenyl groups cannot explain the observed broadening in the π_4–π_6 region, we have to look for another source of this broadening. Such a source could lie in the direct through-space interaction between the two phenyl rings caused primarily by an overlap of the p_z orbitals at C atoms 2' and 2''. In order to estimate the magnitude of this interaction, we calculated the overlap integrals for Slater p orbitals with an exponent of 1.625 with bond lengths of 1.34 Å for the double bond and 1.48 Å for the single bond and assuming that the phenyl groups are ideally planar six-membered-rings with a C–C distance of 1.40 Å, and we obtained the following values for the 2',2'' distances (r) and for the overlap integrals (S'):

θ	Φ	120°	129°	135°	150°
30	r(Å)	2.08	2.72	3.17	4.23
	S'	−0.138	−0.043	−0.018	−0.002
45	r(Å)	2.65	3.23	3.63	
	S'	−0.079	−0.027	−0.011	
60	r(Å)	3.23	3.77	4.13	
	S'	−0.027	−0.009	−0.004	

In this range of Φ and θ, the overlap is primarily a σ-type of overlap.

The value of the overlap integral is 0.217 for two parallel p_z orbitals at a distance of 1.48 (this was bond length to which we had attributed an interaction parameter β_0 of −2.45 eV). Thus, we estimate that the through-space interaction β' between atoms 2' and 2'' is of the order of 10–20% of the interaction parameter β_0 in *cis*-stilbene. When we included an increasing amount of 2'–2'' interaction (β') in the LCMO calculations (Table VII) we found an increasing split between π_4 and π_6. Of special interest is the fact that π_5 and π_6 are no longer degenerate. This is in agreement with the UP spectra of *cis*-stilbene and of all 1,2-diphenylcycloalkenes except **11**. The separation between π_3 and π_7 is nearly independent of β' up to a value of about 0.7 eV which is approximately the upper limit for this kind of through-space interaction.

To summarize the theoretical interpretation of *cis*-stilbene UP spectra, the through-space interaction has little influence on the energy of π_3 and π_7. Thus, the π_3–π_7 separation is influenced primarily by the twist angle of the phenyl group. On the other hand, the π_4–π_6 separation is determined by the amount of through-space interaction of the 2',2'' positions and is largely unaffected by the π interaction along the single bond. Thus, the two effects give a powerful tool for understanding the geometry of the *cis*-stilbene moiety.

Gas-Phase Structure of Diphenylcycloalkenes. From the results of the LCMO calculations shown in Table VII, it is obvious that the observed decrease of the first VIP with decreasing ring size can only be understood as due to changes in the planarity of the systems. For the same values of θ and β', the first VIP follows the trend of the unsubstituted cycloalkene. In each case, the first VIP of the corresponding cycloalkene (Table II) was reduced by 0.5 eV to obtain an estimate for the inductively perturbed π orbital of the double bond. As mentioned above, this might mean a slight overestimation of the inductive effect, but we do not want to introduce too many parameters into our model. The input parameters for the phenyl groups are the same as those used for **5** and **6**.

Diphenylcyclopropene **11** has already been studied by Müller, Schweig, and Vermeer.[37] These authors assumed **11** to be planar or at least nearly planar. Such a planar structure is indeed feasible: in **1**, the angle Φ is 149.9°.[43] From the comparison of ethylene and *cis*-stilbene, we can expect that if this angle is changed at all in the diphenyl derivative, it will be widened. The distance of 2.01 Å between the two ortho hydrogen atoms that is found for a planar structure with Φ = 150°, and the same single and double bond lengths as in **15**,[39] is certainly a lower limit for actual hydrogen/hydrogen distance. The QCFF/PI calculation (Table VI) predicts a twist angle θ = 6°. The result which we obtained from our model calculation for a planar structure of **11** (Table VIII) is in good agreement with the experiment. The separation between π_3 and π_7 is somewhat difficult to extract from the experimental spectrum due to a perturbation in the region of π_3 that has been attributed to the hyperconjugative effect of the methylene group.[37]

11 is the only *cis*-stilbene type system considered in this paper that does not show a broadening in the π_4–π_6 region (compare Figure 3). The UP spectrum in this energy range looks very similar to what we observed for **16**. There is no indication that the near degeneracy of π_5 and π_6 is lifted in this compound. The distance between C atoms 2' and 2'' (3.89 Å for the planar structure) is much too large to allow any significant through-space interaction between the two phenyl rings (see also the overlap integrals, vide supra).

In the four-membered-ring compound **12**, the first VIP is shifted to somewhat higher energies and the π_3–π_7 separation is slightly reduced. Compared to **11** and **16** we observe for the first time a broadening of the π_4–π_6 region with a clearly detectable split of the 9-eV band. The broadening is similar to the one observed in **15** (Figure 3). The force field calculations (Table VI) predict twist angles of about 23° and a bond angle Φ of 136° and 137°, respectively. The latter value is in close agreement with the 136.5° which we found from our X-ray analysis. This signifies that the added repulsions still cause only a very slight opening of the bond angle Φ in **12** compared to **2** where the experimentally observed angle is close to 135°.[26] The two phenyl rings are asymmetrically twisted in the X-ray structure (Table VI), but the average twist angle (21°) compares quite well with the calculated value of 23°. The central double bond is twisted by 10.3°, the largest value found for the three 1,2-diphenylcycloalkenes for which X-ray structures are now available.

From the structural data discussed above, the 2'–2'' interaction is expected to be in the order of 0.2 to 0.3 eV. Indeed, the energies predicted by the LCMO calculations for β' = 0.3 and a twist angle θ of 30° to 40° (Table VII) are again in good agreement with the experimentally observed values (Table V).

For the tetramethyl derivative **12a** the MMP2 calculation predicts a relatively asymmetric structure in which one ring is twisted by 44° and the other by 18°. However, the UP spectrum of **12a** is very similar to the UP spectrum of **12**. The π_3–π_7 separation is somewhat further reduced indicating a structure in which the average twist of the phenyl rings is somewhat larger than in **12**.

The broadening of the π_4–π_6 region in the five-membered-ring compound **13** is more pronounced than in the other systems discussed thus far. π_3 is no longer a separate band but only a shoulder at the high energy side of the broadened π_4–π_6 structure which makes the estimation of the corresponding VIP somewhat uncertain. The given estimate of 9.9 eV is certainly an upper bound, indicating that the torsion of the phenyl groups is more pronounced in **13** than in **12**. The results of the force field calculations match the X-ray data very well (Table VI). Of special interest is the correspondence of the predicted and the observed values for the bond angle Φ and the twist angle Ω around the double bond. In the X-ray structure there is again a tendency for a slight asymmetry in the twist angle of the two phenyl groups and the average twist angle (ca. 46°) is about 10° larger than predicted by the force field calculations. Since the twist angles found in the solid state are usually smaller than those observed

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[43] Stigliani, W. M.; Laurie, V. W.; Li, J. L. *J. Chem. Phys.* **1975**, *62*, 1890.

Table VIII. Data from Electronic Spectra of Compounds **12** to **15**[a]

	compound									
	12		**12a**		**15**		**13**		**14**	
	LNT	TR	LNT	RT	LNT	RT	LNT	RT	LNT	RT
					Absorption					
Ia	30.9 sh	31.1 sh	30.7 sh							
Ib	32.3	32.7 sh	32.3							
Ic	33.7	34.0 (18000)	33.7							
Id	35.1 sh	35.5 sh		36.1 (11800)	35.1	36.6 (10500)	35.1	37.2 (10900)	38.8	37.2 (9100)
$f(1)$	0.47			0.40		0.34		0.32		
II	42.3	42.7 sh (13000)	42.0	42.0 sh (9600)	?	?	42.6 sh	42.4 sh (10500)	43.8 sh	43.1 sh (9500)
IIIa	44.0	44.5 (22500)	43.9	43.5 sh			44.2	44.6 (16500)		
IIIb	45.1	45.3 sh	44.8 sh	44.6 (19200)	44.8	45.2 (21200)	45.2 sh	45.7 sh	45.9	45.0 sh (10600)
onset	29.5	29.5	29.5	29.5	30	30	30	30	33	32.5
					Emission					
onset	29.5		29		28		28			
max	25.8		25.4		23.2		23.8			
	26.6[b]	26.2[b]	26.4[b]	25.5[b]						

[a] All energies are in 10^3 cm^{-1}. ϵ values (in L mol^{-1} cm^{-1}) are given in parentheses. $f(1)$ is the oscillator strength corresponding to the whole area of band I measured from the onset to the minimum between bands I and II. [b] Reference 44.

for the free molecule, it seems that the force field calculations again underestimate the twist angle. Due to the larger twist angle θ and the smaller bond angle Φ, the through-space interaction between the two phenyl rings should be more pronounced in **13** than in **12**. The best fit of the results of the LCMO model with the experimentally observed VIP is obtained for $\theta = 45°$ and $\beta' = 0.7$ eV (Table VII).

It is interesting to note that the energy of the onset of the σ ionizations is always highest for the five-membered-ring compound. This has been previously observed for the unsubstituted cycloalkenes,[22] and it is also found for the monophenyl- and diphenylcycloalkenes.

For the six-membered-ring compound **14** the crystal structure shows asymmetrically twisted phenyl rings but the average twist angle is nearly the same as the one observed for **13**. For the free molecules in the gas phase, such a similarity in the twist angles could not explain why the π_3–π_7 separation is drastically reduced in **14** compared to **13** (compare Table V). Only a twist angle of the order of 50° to 60° is in accordance with this reduced separation (Table VII). The force field calculations, too, predict a twist angle for **14** that is about 10° larger than that for **13**. The half-chair form of the cyclohexene ring adds considerably to the steric interaction between the phenyl group and the cycloalkene ring. Whereas in **15** and in the diphenylcycloalkenes with small rings the nonplanarity of the π system is primarily caused by steric hindrance between the phenyl groups, it is now due in part to the interaction between the phenyl groups and the cycloalkene ring. This observation parallels our observations of the monophenylcycloalkenes. The smaller twist angle found in the crystal structure is most likely due to packing effects as in biphenyl or *trans*-stilbene.

A twist angle of 50° to 60° should lead to a reduced through-space interaction between the two phenyl rings, but this reduction is in part counterbalanced by the smaller bond angle Φ (Table VI). The broadening of the π_4–π_6 region which is characteristic of the through-space interaction seems to be slightly smaller in **14** than in **13**. The theoretical ionization potentials that we obtain from our LCMO model agree well with the experimental results when we include a through-space interaction of $\beta' = 0.5$ eV.

From the combined information derived through X-ray analysis, force field calculations, and UP spectra we conclude that the twist of the phenyl groups increases monotonically in the order **11** < **12** < **12a** < **13** < **14** with **15** most similar to **13**.

Solution-Phase Structure of Diphenylcycloalkenes. Several of the absorption spectra are shown in Figure 5. The relevant data are collected in Table VIII including the maxima of the fluorescence spectra measured at liquid nitrogen temperature. A slight indication of vibrational structure with a spacing of about 900 cm^{-1} is found in the LNT fluorescence spectra of **12** and **12a**. The other fluorescence spectra do not show indications of vibrational structure. For **14** the fluorescence quantum yield seems to be much lower than for the other compounds. With our apparatus we could not detect any measurable emission at liquid nitrogen temperature. In all four cases where we observe an emission the whole emission band and the first absorption band up to about 41 000 cm^{-1} are polarized uniformly. The observed degree of polarization[44] is close to 0.5, indicating that absorption

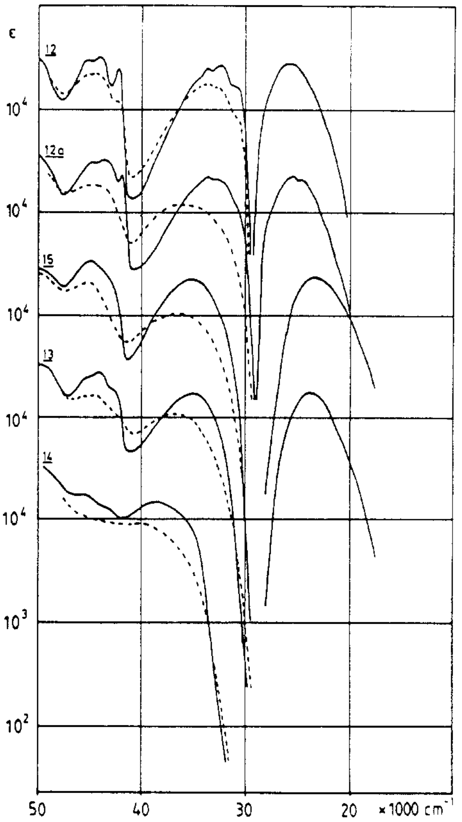

Figure 5. Electronic spectra of *cis*-stilbene (**15**) and several 1,2-diphenylcycloalkenes: (- - -) absorption spectrum at room temperature, (—) absorption and emission spectra at liquid nitrogen temperature.

Table IX. Calculated Excitation Energies (in 10^3 cm^{-1}) and Oscillator Strengths (Values Given in Parentheses) for Different Geometries of **15**[a]

	15	15	15	15	15	15	15	15	13
Φ	128	128	128	128	120	128	128	128	128
Ω	0	0	0	10	0	0	10	0	0
θ	10/80	20/40	30/30	30/30	45/45	45/45	45/45	60/60	45/45
	38.6 (0.004)	31.7 (0.160)	31.5*xz* (0.160)	33.1 (0.280)	31.7 (0.120)	36.5 (0.390)	36.6 (0.440)	38.6 (0.020)	35.8 (0.440)
	39.3 (0.410)	36.1 (0.030)	35.9*xz* (0.030)	36.9 (0.020)	34.7 (0.060)	37.6 (0.006)	37.9 (0.008)	38.7*y* (0.001)	37.2 (0.020)
	39.6 (0.020)	37.6 (0.001)	37.6*y* (0.001)	38.1*yz* (—)	37.1*y* (0.001)	38.2*y* (0.002)	38.2*yz* (0.002)	39.8 (0.340)	37.8 (0.003)
	43.1 (—)	41.6 (0.050)	41.7*y* (0.030)	41.9*yz* (0.030)	39.6*y* (0.050)	41.7*y* (0.020)	41.8*yz* (0.020)	42.2*y* (0.010)	40.9 (0.040)
	45.7 (0.390)	45.0 (0.070)	45.2*xz* (0.380)	45.6 (0.180)	43.8 (0.130)	45.3 (0.270)	45.3 (0.250)	45.2 (0.490)	44.7 (0.250)
	47.5 (0.070)	45.2 (0.430)	45.6*y* (—)	46.0*yz* (—)	46.3*y* (0.004)	46.9*y* (0.006)	46.7*yz* (0.005)	48.6*y* (0.007)	45.6 (0.010)
	49.8 (0.640)	47.1 (0.790)	45.7*xz* (0.980)	48.0 (0.940)	49.1 (0.830)	49.8 (0.620)	50.1 (0.330)	51.0 (0.020)	47.9 (0.120)
	52.4 (0.080)	50.1 (0.030)	49.9*xz* (0.030)	50.3 (0.030)	50.3 (0.270)	50.6 (0.220)	50.9 (0.310)	52.3*y* (0.020)	48.7 (0.280)

[a] For the definition of the coordinate system and the angles Φ, Ω, and Θ, see Table VII. (—) shows oscillator strength $<10^{-3}$.

and emission are polarized parallel as expected for normal fluorescence. Absorption and emission spectra at RT of **12** and **12a** have already been measured by Kaupp and Stark.[45] These authors report that both compounds are strongly fluorescent also at room temperature (see Table VIII).

The main features observed throughout the entire series of investigated compounds including **15** are as follows:

(i) In the RT as well as in the LNT spectra, the maximum of the first absorption band shifts gradually toward higher energies when we go from **12** to **14**.

(ii) The fluorescence maximum is shifted to lower energies in the same order, increasing the Stokes shift from 6500 cm^{-1} in **12** to 11300 cm^{-1} in **13**.

(iii) The onset of the absorption spectrum lies approximately at the same energy for **12**, **12a**, **13**, and **15** but is shifted about 2000 cm^{-1} to higher energies when we go to **14**.

(iv) The maximum of the first absorption band shows the strong low-energy shift with decreasing temperature that is well-known for sterically hindered *trans*-stilbenes.[46] The shift is most pronounced for **12a**. From the spectra of **12** where vibrational fine structure is indicated in the RT spectrum and resolved in the LNT spectrum it is obvious that this shift is caused by a change in the Franck-Condon factors of the vibrational subbands. At room temperature the maximum corresponds to the 0–2 transition of a well-detectable 1400-cm^{-1} progression. At LNT the maximum is shifted to the 0–1 transitions.

(v) As in **16**, two further bands (labeled II and III in Table VIII) are observed between 240 and 210 nm in all five compounds. The position of these bands changes very little with the nature of the compounds and it shows almost no temperature dependence.

The first absorption band in stilbene systems is certainly a "conjugation band". The energy and intensity of this band strongly depend on the geometry of the π system. Increasing twist of the phenyl rings leads to a reduction of the π interaction between the phenyl rings and the double bond and causes a high-energy shift of the first π–π^* transition. Bands II and III, however, result from transitions that are highly localized in the phenyl rings.[9] Their energy is expected to be relatively independant of the twist angle. These qualitative expectations are fully confirmed by the results of our CNDO/S calculations (Table IX). For the same bond angle Φ, the conjugation band is shifted by about 8000 cm^{-1} to higher energies when we increase the twist angle θ from 30° to 60°. For $\theta = 60°$ and $\Phi = 128°$ the conjugation band no longer corresponds to the first π–π^* transition. For large twist angles the local L_b-type excitations of the phenyl rings[9] become the lowest ones. Surprisingly, the calculated oscillator strength of the conjugation band does not decrease monotonically with increasing θ. For constant values of Φ and Ω, it rises up to $\theta = 45°$ and then drops only little.

The second transition that has a calculated oscillator strength larger than 0.1 is predicted around 45 000 cm^{-1}. This transition shows very little sensitivity with respect to changes in Φ and θ. A slight asymmetry in the twist of the two phenyl groups up to ±15° leads to results which deviate very little from those observed for a symmetric twist around the average angle. Strongly asymmetric twist angles, however, lead to results that differ considerably from those obtained for a comparable symmetric twist. Inclusion of a twist around the double bond of 10° has little influence on the results. Contrary to this, a considerable influence is found when we change the bond angle between the double and the single bond (Φ). A reduction of Φ from 128° to 120° leads to a low energy shift of about 4000 cm^{-1}. The result found for $\Phi = 120°$ and $\theta = 45°$ is very similar to the result found for $\Phi = 128°$ and $\theta = 30°$. The inductive effect of the alicyclic ring is also predicted to be negligible. The result is nearly unchanged as long as we do not alter the geometry of the *cis*-stilbene moiety. This is shown in Table IX for the example of **13**.

The strong temperature dependence of the maximum of the first absorption band has been explained by Bromberg and Muszkat.[46] It is due to a strong asymmetry of the potential with respect to the twist angle θ. For larger twist angles θ the potential is mainly governed by the decrease in π interaction between the double bond and the phenyl ring which leads to a $\cos^2\theta$ type of potential. For small twist angles θ the repulsive potential is mainly due to steric interaction which leads to a steep Lenard-Jones potential. For such a strongly asymmetric potential the average twist angle increases considerably with increasing temperature. When we compare calculated and observed excitation energies we therefore refer to the energies measured at LNT, since these are more closely related to the geometry which is used for the calculations.

In Table X, we show calculated excitation energies and oscillator strengths for the experimentally investigated compounds, mostly based on the optimized geometries that result from the QCFF/PI force field calculations. As mentioned above these geometries are close to the experimentally observed geometries for those compounds where experimental information is available. Nonnegligible deviations are only observed for the twist angles θ_1 and θ_2.

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(44) Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light*; VCH Publishers: New York, 1986.

(45) Kaupp, G.; Stark, M. *Chem. Ber.* **1978**, *111*, 3608.

(46) Bromberg, A.; Muszkat, K. A. *Tetrahedron* **1972**, *28*, 1265.

Table X. Calculated Excitation Energies (in 10^3 cm^{-1}) and Oscillator Strengths for *cis*-Stilbene **15** and Several 1,2-Diphenylcycloalkenes[a]

compd	**11**	**12**	**15**	**13**	**13**	**14**
θ (deg)	7	23	38	35	45	45
	30.1 (0.830)	31.9 (0.480)	33.2 (0.150)	31.8 (0.200)	35.8 (0.440)	36.9 (0.240)
	35.1*y* (0.010)	36.1 (0.020)	36.7 (0.030)	35.8 (0.050)	37.2 (0.020)	37.2 (0.050)
	35.2*y* (0.010)	36.4*y* (0.004)	38.1*y* (0.001)	37.2 (—)	37.8 (0.003)	38.1*y* (0.010)
	39.0*y* (0.020)	40.6*y* (0.030)	42.1*y* (0.030)	40.7 (0.050)	40.9 (0.040)	40.9*y* (0.030)
	43.1 (0.002)	43.8*y* (0.001)	45.4 (0.340)	44.3 (0.400)	44.7 (0.250)	44.6 (0.330)
	44.3 (0.005)	44.8 (0.130)	46.9*y* (0.002)	44.7 (0.002)	45.6 (0.010)	47.8*y* (0.040)
	44.4 (0.080)	45.8 (0.630)	47.8 (0.990)	46.0 (0.620)	47.9 (0.120)	48.7 (0.160)
	45.7*y* (0.240)	47.1 (0.160)	50.6 (0.060)	48.0 (0.140)	48.7 (0.280)	49.5 (0.380)
	46.2*y* (0.040)	47.9*y* (0.150)		48.8 (0.020)	49.3 (0.020)	50.5*y* (0.010)
	46.5 (0.220)	49.6 (0.010)				

[a] The phenyl rings are twisted symmetrically by θ. All other structural parameters correspond to the result of the QCFF/PI calculation.

No comparison is possible for **11**, since we did not find information on the UV spectrum of this compound in the literature. If the predictions from the calculations are reliable, then the first band of **11** should be shifted somewhat to the red, compared to **12**, and it should be about twice as intense. For **12** the results of the CNDO/S calculations are in excellent agreement with the experimental results. We assign the first band to the first calculated transition which is predicted to lie vertically at 31 900 cm^{-1}. Band II of the experimental spectrum is assigned to the sixth excited state (calculated oscillator strength of 0.13). Band IIIa is assigned to the seventh excited state, the predicted oscillator strength of which is about one-third higher than the oscillator strength of the first transition, in good agreement with the experimentally observed intensities. Band IIIb may be connected with the 8th excited state which also has a reasonable oscillator strength. The fact that the energy difference between bands IIIa and IIIb differs somewhat between LNT and RT spectra makes it feasible that the IIIa and IIIb are not subbands of the same electronic transitions, but instead are bands that belong to different electronic excitations.

In **15** the first transition is shifted to higher energies in accordance with the experimental findings. The predicted oscillator strength is considerably lower than the one found for **12**. Such a strong decrease is not observed in the experimental spectrum. The high energy shift and the oscillator strength are increased when the phenyl groups are twisted somewhat more strongly. This is again an indication that the QCFF/PI calculations underestimate twist angles, a conclusion already drawn from the UP spectra.

For **13** the structure obtained from the QCFF/PI calculation leads to a first transition that is similar in energy to the one observed in **12**. The similar high energy shift of the first band observed for **13** and **15** is not described by this calculation. When we keep the same structural parameters but increase the twist angle from 35° as predicted by the QCFF/PI calculations to 45° we observe a considerable high energy shift of 4000 cm^{-1} and an increase of the calculated oscillator strength by a factor of about 2. Comparison with the experimental data makes it more feasible that the average twist angle in **3** is somewhere between 40° and 45°, a value that is very close to the one suggested from the UP results.

For **14**, a CNDO/S calculation based on the QCFF/PI geometry, but with the twist angles (θ_1 and θ_2) increased to 55° as suggested by the UP spectral results, predicts that the conjugation band will still be the lowest energy band (Table X). This calculation also predicts a markedly reduced intensity for the bands in the 44 000 to 50 000 cm^{-1} energy range. This agrees quite well with the fact that band III of **14** has a much lower intensity than the corresponding band in the other compounds investigated in this study. Surprisingly, **14** has a much lower fluorescence quantum yield than the other compounds in this study by a factor of 10–50 times. One possible explanation for the diminished quantum yield derives from a change in the lowest energy excited state. This situation would result from a state with primarily benzene L_b character dropping in energy relative to the conjugation band. Due to the diminished oscillator strength of the L_b state, this should have a radiative lifetime 10 to 100 times longer than the state connected to the conjugation bond. An alternative rationale for the diminished fluorescence quantum yield for **14** derives from the increased flexibility of **14**. The increased flexibility may allow sufficient twisting of the double bond to allow a new excited state deactivation pathway to become operative. Such an effect has been previously observed for the monophenylcycloalkenes.[47] The excited-state lifetimes for **13** and **14** have been found to be ≤20 ps.[2a] Thus, with the presently available data, it is impossible to discriminate between these alternative rationales.

The results obtained from the investigation of the UV spectra parallel those derived from the UP spectra. The twist of the phenyl groups in 1,2-diphenylcycloalkenes increases in the order **11** < **12** < **12a** < **13** < **14** with unsubstituted *cis*-stilbene (**15**) most similar to the five-membered-ring compound **13** as far as the geometry of the *cis*-stilbene moiety is concerned.

V. Conclusion

From the combined information of UP and electronic spectra, we find that the 1,2-diphenylcycloalkenes become increasingly nonplanar in the order **11** < **12** < **13** < **14**. Whereas **11** is nearly planar, the phenyl rings in **14** are twisted by about 45° to 55° depending on whether the molecule is in the solid state or in the gas phase. Introduction of four methyl substituents in the four-membered ring (**12a**) leads to a slight increase of the torsion of the phenyl rings. *cis*-Stilbene (**15**) is most similar to the five-membered-ring compound (**15**) as far as the geometry of the stilbene moiety is concerned.

The increasing twist of the phenyl groups together with a decrease of the bond angle between the double and the single bond leads to an increasing through-space interaction between the two phenyl rings that is pronounced most in the five-membered-ring compound. The decrease in π interaction along the single bonds overcomes the inductive effect of the alicyclic ring in that the first ionization potential of the 1,2-diphenylcycloalkenes increases in the order **12** < **14** whereas the IPs of the unsubstituted cycloalkenes decrease in the same order. For the monophenylcycloalkenes included in this study the first IP goes through a minimum for the five-membered-ring compound.

The structures inferred from the UP and electronic spectra are in close agreement with the structures derived from crystal structure analysis for **12**, **13**, and **14**. Only for the six-membered-ring compound **14** the twist of the phenyl groups seems to be less pronounced in the solid state than in the gas phase. In **12**, **13**, and **15**, the steric hindrance that leads to nonplanarity is mainly due to the steric interaction between the two phenyl rings. This interaction is too strong to be overcome by a gain in lattice energy that would result from a more planar structure. In biphenyl and in *trans*-stilbene the steric hindrance is due to hydrogen/hydrogen interactions. This kind of interaction is weak enough to be overcome in the solid state. In **14** the nonplanarity is caused by interaction of the phenyl groups with the acyclic ring, in addition to the normal ring/ring interaction of the phenyl groups. The former interaction may be partly overcome when we go from

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[47] Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718.

the gas phase to the solid thus explaining the structure difference in this case.

Force field calculations predict the structures of **11**, **12**, **13**, **14**, and **15** astonishingly well. Both the bond angle Φ and the twist angle θ are predicted in such a way that the resulting geometries are in full agreement with what we inferred from the UP and electronic spectra. This finding contrasts with previous observations for *trans*-stilbene in which the force field calculations were not able to describe the nonplanar structure of the free molecule in the gas phase. The force field methods also fail to predict the nonplanar structure of the larger monophenylcycloalkenes. As in the case of *trans*-stilbene the nonplanarity of these monophenylcycloalkenes seems to be caused by improper balancing of the weak hydrogen/hydrogen interactions and the resonance interactions. These compounds provide a substantial test for the balance of these forces. Presently available force-field methods seem not to be optimized properly for this balance.

Semiempirical quantum chemical methods like MNDO, MINDO, and even MNDOC (including second-order Møller–Plesset corrections) all overestimate the twist angles in these loosely coupled π systems, either by overestimating the repulsive forces or by underestimating the stabilization resulting from π-electron delocalization.

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Registry No. 1, 2781-85-3; **2**, 822-35-5; **3**, 142-29-0; **4**, 110-83-8; **5**, 3618-12-0; **6**, 100-42-5; **7**, 86659-36-1; **8**, 3365-26-2; **9**, 825-54-7; **10**, 771-98-2; **11**, 24168-52-3; **12**, 3306-02-3; **12a**, 20396-46-7; **13**, 1485-98-9; **14**, 41317-87-7; **15**, 645-49-8; **16**, 103-30-0; **17**, 1860-17-9; **18**, 18869-29-9; **19**, 1694-19-5; **20**, 15638-14-9; **21**, 2510-75-0.

Supplementary Material Available: The molecular structure and tables of positional parameters, general temperature factor expression, and bond distances and angles for 1,2-diphenylcyclohexene (**14**) (8 pages); listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Rate Constants for Reactions in Viscous Media: Correlation between the Viscosity of the Solvent and the Rate Constant of the Diffusion-Controlled Reactions[1]

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Abstract: The kinetics of the quenching of excited pyrene by several molecules in a variety of hydrocarbon solvents and in a diol are reported. The rate constants for reaction of the excited pyrene are, for the most part, diffusion-controlled and considerably faster than those calculated by use of the Smoluchowski and Stokes–Einstein equations. Measurements of the diffusion constants of the reactants and direct use of the Smoluchowski equation does predict rate constants that are in agreement with those measured. Application of the Stokes–Einstein equation shows that this equation does not calculate the correct diffusion constant for the reactants in the media studied. A free volume theory with transition-state concepts suggests that the diffusion constants of reactants in the liquids used vary as the increase of the square root of the bulk viscosity. This is in very good agreement with the experimental findings. A discussion of what the data mean for diffusion-controlled reactions involving electron transfer and complex formation is included, and also hinted at is the implication of the data for reactions in micelles and vesicles.

A diffusion-controlled reaction is defined as one occurring at each encounter of the reactants. The theory of such reactions has been developed by Smoluchowski,[2] Collins and Kimball,[3] Noyes,[4] and others, and the subject has been reviewed by Noyes,[4] Birks et al.,[5] and recently by Rice.[6]

The smoluchowski equation in its simplest form, i.e. when transient terms are disregarded, is given below:

$$k = 4\pi N'RD \tag{1}$$

where k is the rate constant of the bimolecular process in units $M^{-1}\ s^{-1}$, N' is Avogadro's number per millimole, R represents the encounter distance taken as the sum of the molecular radii, and D is the relative diffusion coefficient ($D = D_A + D_B$).

For a particle moving in a continuous medium the diffusion coefficient is given by

$$D = kT/f \tag{2}$$

where k is the Boltzmann constant and f is the friction coefficient. The friction coefficient has been calculated by Stokes, for a sphere of radius r, moving in a continuum of viscosity η and is given by[7]

$$f = 6\pi\eta r \frac{1 + 2\eta/\beta r}{1 + 3\eta/\beta r} \tag{3}$$

where β is the coefficient of sliding friction between the diffusing molecule and its surroundings. If the dimensions of the moving molecule are large compared with those of the solvent molecules, then $\beta = \infty$ and no slipping occurs. In such a case, $f = 6\pi\eta r$ and the diffusion coefficient is given by the known Stokes–Einstein equation:

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(2) Smoluchowski, M. V. *Physik. Chim.* **1917**, *92*, 124.

(3) Collins, F. C.; Kimball, G. E. *J. Colloid. Sci.* **1917**, *4*, 425.

(4) Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129.

(5) Alwattar, A. H.; Lumb, M. D.; Birks, J. B. *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1973; Vol. 1, pp 403–454.

(6) Rice, S. A. *Comprehensive Chemical Kinetics*; ed. C. H. Bamford, C. H., Compton, R. G., Ed.; Elsevier: New York, 1985; Vol. 25.

(7) Stokes, G. G. *Mathematical and Physical Paper*; Cambridge University: London, 1903; Vol. 3, pp 55.

0002-7863/88/1510-4494$01.50/0