Theoret. chim. Acta (Berl.) 1, 294—301 (1963)

Institute of Physical Chemistry, University of Milan, Italy

Molecular Geometry of Phenyl- and Methyl-Substituted Ethylenes

By

GIORGIO FAVINI and MASSIMO SIMONETTA

By using a very simplified method for determining the deformation and repulsion energy, the most stable geometrical structure was calculated for each molecule obtainable from styrene substituting one or more hydrogen atoms with methyl or phenyl groups.

The frequency and the oscillator strength for the $\pi - \pi'$ electronic transition were determined for the molecules in the calculated geometry.

The results are in no bad agreement with the experimental data.

Unter Verwendung einer einfachen Näherungsmethode zur Bestimmung der Deformations- und Abstoßungsenergie wurde die stabilste geometrische Molekülstruktur einiger Styrolderivate berechnet. Es handelt sich um Verbindungen, die sich vom Styrol durch Ersatz eines oder mehrerer äthenkohlenstoffständiger Wasserstoffatome durch Methyl- oder Phenylgruppen ableiten.

Die Frequenzen und Oszillatorenstärken der $\pi - \pi'$-Elektronenübergänge werden für die ermittelten Molekülgeometrien angegeben.

Berechnete und experimentelle Werte stimmen nicht schlecht überein.

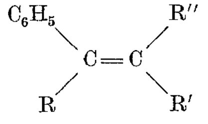
A l'aide d'une méthode très simplifiée pour la détermination des énergies de déformation et de répulsion, la structure stérique la plus stable a été calculée pour tous les dérivés du styrène qu'on obtient en substituant un ou deux atomes d'hydrogène par des groupes méthyl ou phényl.

La fréquence et la force oscillatrice de la transition électronique $\pi - \pi'$ ont été déterminées pour les géométries calculées des molécules.

Les résultats ne s'accordent pas mal avec les données expérimentales.

In the last few years, the problem of the interaction of non-bonded atoms or groups in the same molecule has been the object of numerous investigations [*1, 12, 15, 20*]. The introduction of electronic computers made the calculation of the most stable molecular structure possible, even for complex molecules [*12*]. Most interesting are the cases where the interaction forces result in a deformation of the molecular structure from what we would expect as a result of the bonding forces alone; a typical example is that of conjugated molecules changing their planar configuration.

COULSON [*5*] considered three types of non-planar conjugated molecules: the polyphenyl, polynuclear and corrugated-ring molecules. Another case of conjugated molecules undergoing steric deformation is that of ethylene derivatives containing at least one phenyl group bonded with an ethylenic carbon atom:



(I)

The scope of this work is to determine the deformation of molecules of type (I) theoretically; R, R' and R'' may be a hydrogen atom, a methyl or a phenyl group.

Furthermore, the theoretical results were compared with the molecular structure deducted from the study of the ultraviolet spectra of these substances.

General method

Owing to the complex structure of the molecules in question, we had to choose among many parameters. Therefore, only deformations whose effect in diminishing the steric interaction was prominent were considered. Among these only those with a low energy cost were included in the calculation. On this basis, deformations of the bonds due to bond-stretching were excluded, because the stretching force constants are considerably higher than the bending or the twisting force constants [*34*]. Among the deformations due to twisting, rotation around the phenyl-ethylenic carbon bonds was included, while rotation around the ethylenic bond was neglected. In the bending deformations, we included only the in-plane variation of the angles whose vertices bear an ethylenic carbon atom.

Three terms were taken in consideration: the π-electron energy, the repulsion-energy of the atoms whose distance is smaller than the "touching" distance, and the bending-energy of the bonds.

The calculation for each molecule was started on a hypothetical planar structure, where the steric interactions were disregarded; for the other configurations, the energy variation caused by twisting and bending deformations and the steric repulsion energy were determined. The difference E between the hypothetical structure's energy and the deformated structure's energy corresponds to the steric energy as defined by HILL [*13*] apart from zero point energy's differences.

A. Starting from conventional data, the initial planar structure was determined by applying the molecular orbital method in Hückel approximation, without inclusion of overlap integrals: we thus obtained the bond orders, from which bond distances were determined using COULSON's formula [*4*]. From the latter distances new values for the exchange integrals β were obtained and the calculation was repeated until a consistent value was reached ($\Delta r \leq 0.005$ Å). Hence, we obtained the interatomic distances for an assumed planar molecule, and with a rather arbitrary value of 120° for $sp^2 — sp^2$ bond angles. In order to consider the variation of β with respect to the distance $C — C$, several curves or equations have been suggested [*27*]; the calculations shown here have been made using the values of MULLIKEN and others [*18*], while the formula $\beta = k\,S$ ($S =$ overlap integral) should rather be used in relation to its consistency with the formula for the variation of β due to twisting (see paragraph **D**). However, the choice of the curve $\beta = f(r)$ does not affect considerably the final results. For molecules containing one or more methyl groups, the L. C. SNYDER method [*26*] was used, giving the parameters the following values:

$$\alpha_{CH_3} = \alpha_C + 3.3\,\beta_0 \qquad\qquad \beta_{C-CH_3} = 0.8\,\beta_0$$

where β_0 is the resonance integral for benzene taken as —20 Kcal/mole.

B. In each case, the repulsion energy for pairs of atoms having a distance smaller than the "touching" distance was calculated using the KITAYGORODSKY formula [*15*]:

$$E_S = -0.14\left(\frac{r_0}{r}\right)^6 - 3.10^4\, e^{-13\frac{r}{r_0}}$$

where r is the actual distance and r_0 the "touching" distance, obtained by adding Van der Waals' atomic radii. The values of the radii have been taken from PAULING's Table [*21*] and corrected according to DOSTROVSKY, HUGHES and INGOLD [*9*] when the line joining the two atoms and the direction of the nearest bond make an angle smaller than 90°.

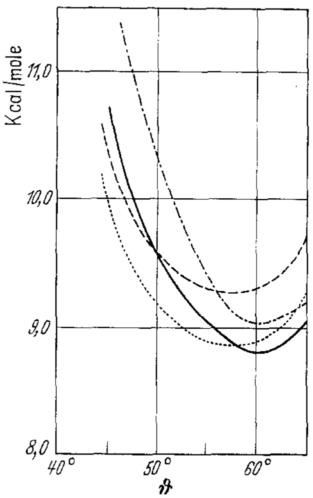


Fig. 1. Steric energy of 2,2-dimethyl-1,1-diphenylethylene; — · — · — · $\alpha = \beta = 120°$; $\gamma = \delta = 120°$; ———— $\alpha = \beta = 117.5°$; $\gamma = \delta = 120°$; · · · · · · · $\alpha = \beta = 117.5°$; $\gamma = \delta = 117.5°$; — — — — $\alpha = \beta = 115°$; $\gamma = \delta = 120°$

C. The bending energy in the plane of the bonds has been determined by the formula

$$E = \frac{1}{2} k (\alpha - \alpha_0)^2$$

where $\alpha_0 = 120°$ and k is the force constant. The force constant values for the deformation of the angles $C = C\diagup^{H}$ and $C = C\diagup^{C_{\text{aliph}}}$ have been taken from the literature [*33*]. As for the angle $C = C\diagup^{C_{\text{ar}}}$ k was calculated by an approximated method [*32*] starting from the three stretching and bending frequencies of styrene given in the literature [*22*]: the result is $k = 1.35 \cdot 10^{-11}$ dyne/cm · rad^2 and the same value was obtained from the propylene and styrene bending frequencies, assuming that force constants are proportional to the square of the frequencies.

D. The energy variation of the π-electrons, as a result of the twisting of the phenyl groups, was calculated assuming, for the resonance integral of the bond where the twisting takes place, the equation: $\beta_\vartheta = \beta_{\vartheta=0} \cdot \cos\vartheta$ where ϑ is the twisting angle. As usual, the energy of the π-electrons was calculated as the sum of the energies of the occupied molecular orbitals, each energy being multiplied by the number of electrons in the corresponding orbital.

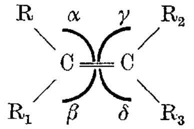
E. Using the energy values calculated in **B**, **C** and **D**, diagrams were drawn which enabled us to locate the most stable configuration, in our approximation. For example, Fig. 1 shows the curves of steric energy for the molecule of 2,2-dimethyl-1,1-diphenyl-ethylene; because of the symmetry of the molecule, the angle ϑ is the same for either phenyl group and the diagram is simpler. When ϑ varies, the bond distances vary accordingly. In particular, the "single" bond becomes longer and the ethylenic bond becomes shorter (see Tab. 1) while the distances in the benzenic rings and the distance between ethylenic and methylic carbon (when this is present) remain practically unchanged. Therefore, the calculation should be done over again starting from the corrected values of the distances. This was done only for those molecules which, owing to a high value of the angle ϑ and to a considerable variation in the bond distances, would presumably bear a considerable change in their final geometrical structure.

In every case, the geometrical variations obtained after consistency was reached, resulted in exeedingly small figures (for example the variation of the angle ϑ did not exceed $\pm$ 1°). This is far below the limit of accuracy for an approximate calculation such as ours. Therefore, the values obtained from the first calculations were chosen as final values for all the molecules. The geometrical

Table 1

Compound (a)	methyl groups	phenyl groups	Bond lengths for the equilibrium configuration (Å)					ϑ (°)	E $\left(\frac{\text{Kcal}}{\text{mole}}\right)$
			$C=C$	$C—R$	$C—R_1$	$C—R_2$	$C—R_3$		
styrene (b)	—	R	1.336	1.474				26	1.63
α-methyl-styrene	R_1	R	1.339	1.479				32	2.59
cis-β-methylstyrene	R_2	R	1.343	1.494				55	4.31
trans-β-methylstyrene	R_3	R	1.340	1.474				26	1.77
cis-2-phenyl-2-butene	$R_1 R_3$	R	1.341	1.478				33	3.76
trans-2-phenyl-2-butene	$R_1 R_2$	R	1.337	1.500				59	4.56
ββ-dimethylstyrene	$R_2 R_3$	R	1.340	1.493				55	4.79
αββ-trimethylstyrene	$R_1 R_2 R_3$	R	1.340	1.501				60	6.26
trans-stilbene (c)	—	$R R_3$	1.346	1.466			1.466	17	3.60
cis-stilbene	—	$R R_2$	1.340	1.480		1.480		43	5.66
trans-α-methylstilbene	R_1	R	1.342	1.490				40	8.02
		R_3					1.488	50	
cis-α-methylstilbene	R_1	R	1.342	1.490				50	6.01
		R_2				1.479		40	
trans-αα′-dimethyl-stilbene	$R_1 R_2$	$R R_3$	1.326	1.500			1.500	62	10.02
cis-αα′-dimethylstilbene	$R_1 R_3$	$R R_2$	1.326	1.484		1.484		46	7.54
1,1-diphenylethylene (d)	—	$R R_1$	1.341	1.481	1.481			33	3.36
2-methyl-1,1-diphenyl-ethylene	R_2	R	1.341	1.502				60	5.99
		R_1			1.476			30	
2,2-dimethyl-1,1-di-phenylethylene	$R_2 R_3$	$R R_1$	1.341	1.501	1.501			60	8.79
triphenylethylene (e)	—	R	1.346	1.484				45	7.04
		R_1			1.473			30	
		R_2				1.477		40	
methyl-triphenyl-ethylene	R_3	R	1.344	1.470				30	10.32
		R_1			1.505			60	
		R_2				1.499		60	
tetraphenylethylene (f)	—	$R_1 R_2 R_3$	1.330	1.489	1.489	1.489	1.489	42	11.12

(a) general formula



(b) bond lengths of planar structure (Å): 1.35 ($C=C$); 1.47 ($C-R$)
(c) bond lengths of planar structure (Å): 1.35 ($C=C$); 1.46 (C — phenyl)
(d) bond lengths of planar structure (Å): 1.35 ($C=C$); 1.47 ($C-R$) ($C-R_1$)
(e) bond lengths of planar structure (Å): 1.355 ($C=C$); 1.46 ($C-R_2$); 1.465 ($C-R$) ($C-R_1$)
(f) bond lengths of planar structure (Å): 1.365 ($C=C$); 1.470 (C — phenyl)

parameters and the steric energy are shown in Tab. 1; deviations of the planar angles from 120° are not shown, as they in every case resulted below our limit of accuracy.

Discussion

It would be very interesting to compare the calculated geometrical structures with experimental data. Unfortunately this is not possible for the lack of experimental data and only an indirect comparison, through the examination of the ultraviolet spectra of these substances will be shown in the following heading.

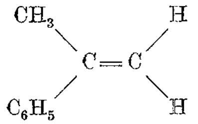
The only known experiment is the *X*-Ray study of trans-stilbene crystals made by ROBERTSON and WOODWARD [*24*]; they found that the asymmetric unit of the crystal contains two different molecules, in which the twisting angle of the phenyl group in respect to the plane of the $CH = CH$ groups is 10.4° and 2.8° respectively. The angle found here is 17°, but it is known that in a crystal lattice forces may produce a considerable variation of the twisting angles. For example, the diphenyl molecule lies in a plane when in the crystalline state [*7*], while the two phenyl groups are twisted by $45° \pm 10°$ when in the vapour phase [*3*].

In the group of the stilbene derivatives, it was found that the twisting angle ϑ in the cis-stilbene is greater than in the trans-stilbene, while the reverse is true in the α, α'-dimethyl derivatives. From the study of the α-monomethyl-stilbenes it appears that the α-methyl group interacts more strongly with the α' than with the α-phenyl group.

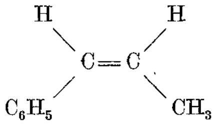
From the present calculations, an approximate value for the energy of cis-trans stilbene isomerisation may be obtained: assuming no energy difference between the isomers in their hypothetical planar structures, the difference in energy between the two molecules in their most stable structure is found as 2.06 Kcal/mole; the experimental value estimated from the data of the isomerisation thermal equilibrium [*14*] is 3 Kcal/mole. The agreement seems satisfactory as the difference in energy between the two hypothetical planar molecules should be added to the theoretical value.

The styrene derivatives can be divided in four groups: 1. derivatives without methyl groups in the α or cis-β positions (cis with respect to the phenyl): the twisting angle is 26°; 2. compounds with one methyl group in the α position and one hydrogen atom in the cis-β position: the twisting angle is 32—33°; 3. derivatives with one methyl group in the cis-β position and one hydrogen atom in the α position: the twisting angle is 55°; 4. derivatives with methyl groups both in the α and cis-β positions: the angle ϑ is about 60°. Therefore the phenyl group shows a stronger interaction with the methyl group in the cis-β position, a lesser one with an α-methyl and pratically no interaction with a trans-β methyl group.

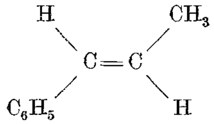
Using the same approximation as for the stilbene, we found that the molecule of cis-2-phenyl-2-butene is more stable than the trans isomer by 0.8 Kcal/mole. The corresponding experimental value is not available, but from the composition of the mixture when in equilibrium [*6*], a difference in free energy of the two isomers of 0.52 Kcal/mole can be calculated. The sequence of the heats of formation in Kcal/mole [*35*] for a), b), c) is at variance



a) $\Delta H_{298} = 27.0$



b) $\Delta H_{298} = 29.0$



c) $\Delta H_{298} = 28.0$

with our E values, but the differences are small enough to be covered by the accuracy of our calculations.

A similar procedure can be applied to the derivatives of 1,1-diphenylethylene. By comparing these compounds with the tri- and tetra-phenylderivatives, it appears that the steric interaction between two phenyl groups separated by a double bond is smaller than between a phenyl and a methyl group in the same positions, while such interactions are almost coincident when the two groups are bonded to the same carbon atom.

Electronic spectra

Since the ultraviolet absorption spectra in solution of all the molecules under consideration are known, we calculated, for the most stable geometrical structure, the energy corresponding to the transition of an electron from the highest occupied molecular orbital in the normal state, to the lowest empty orbital. Such energies are expressed in β units. To obtain the frequency of the maximum in the corresponding band we chose those values of β for which the calculated frequency was equal to the experimental value found for the styrene, trans-stilbene and 1,1-diphenylethylene molecules.

Furthermore, using the MULLIKEN and RIEKE method [*19*], we calculated the oscillator strength for the same transition. Our results, together with those found experimentally, are shown in Tab. 2. The wavenumber variations agree fairly well with the experimental data, with the exception of the cis-2-phenyl-2-butene, for which our theory gives a bathochrome effect of about 1000 cm^{-1}, while the experimental effect has the same magnitude but the opposite direction. However, the separation of the cis and trans isomers through fractional distillation, although performed very carefully, might have not splitted a possible azeotrope, rich in the less volatile component.

In addition, the introduction of one or two methyl groups in the molecule of 1,1-diphenylethylene, does not cause any displacement of the first absorption band of these substances, whereas our theory foretells a hypsochrome effect.

As a whole, the agreement may be deemed to be satisfactory, in consideration of the following points: a) ours was a simplified theory; b) Hückel's method is not the most suitable method for determining the electronic transition energies; and c) the solvent effect was not taken into consideration.

The comparison between the theoretical and the experimental "f" values may also be considered satisfactory, bearing in mind the inaccuracy which takes place when evaluating graphically the experimental data, and the approximation of the theoretical method when calculating the transition moments. The theoretical values are all higher than the experimental ones, as it generally happens in these cases. The ratios between experimental and theoretical values vary between fairly narrow limits. It is known [*16*], however, that *f* values depend largely on the shape of the potential energy curve and not only on ϑ.

Discussions about the influence of displacement from planarity on the absorption spectra of conjugated molecules, have already appeared in the literature [*10, 11, 16*]; in particular Suzuki [*29, 30, 31*] found the twisting angle of the phenyl groups in molecules of type (I) from the study of their spectra. When many nonsymmetrical phenyl groups are present, Suzuki's method determines only an average of the twisting angles. Since Suzuki assumed that the styrene and the trans-stilbene molecules were planar, we recalculated Suzuki's angles starting from styrene with $\vartheta = 26°$ and from trans-stilbene with $\vartheta = 17°$. The results are also shown in Tab. 2.

Table 2

Compound	$\Delta E(\beta)$	ν (cm^{-1})		$\Delta\nu$ (cm^{-1})		f			ϑ (°)	
		theor.	exp.	theor.	exp.	theor.	exp.	theor. corr.	a	b
styrene	1.653	40320	40320[*25*]	—	—	0.57	0.34	0.34	26	26
α-methylstyrene	1.659	40470	40990[*31*]	+ 150	+ 670	0.73	0.49	0.44	32	36
cis-β-methylstyrene	1.768	43130	41560[*17*]	+2810	+1240	0.62	—	—	55	41
trans-β-methylstyrene	1.626	39660	40000[*17*]	— 660	— 320	0.91	0.39	0.54	26	26
cis-2-phenyl-2-butene	1.610	39270	41150[*6*]	—1050	+ 830	0.72	0.42	0.43	33	39
trans-2-phenyl-2-butene	1.742	42500	42555[*6*]	+2180	+2235	0.53	0.22	0.32	59	50
$\beta\beta$-dimethylstyrene	1.723	42015	41770[*31*]	+1695	+1450	0.59	0.40	0.35	55	44
$\alpha\beta\beta$-trimethylstyrene	1.686	41110	42050[*31*]	+ 790	+1730	1.00	0.51	0.60	60	48
trans-stilbene	1.335	34000	34000[*29*]	—	—	1.18	0.62	0.62	17	17
cis-stilbene	1.486	37840	35970[*8*]	+3840	+1970	0.63	0.39	0.33	43	34
trans-α-methylstilbene	1.501	38220	36760[*28*]	+4220	+2760	0.75	0.52	0.39	40 50	39
cis-α-methylstilbene	1.499	38170	37450[*28*]	+4170	+3450	0.31	0.25	0.16	50 40	43
trans-$\alpha\alpha'$-dimethylstilbene	1.615	41130	41070[*28*]	+7130	+7070	0.70	0.35	0.37	62	60
cis-$\alpha\alpha'$-dimethylstilbene	1.462	37240	39700[*28*]	+3240	+5700	0.55	0.37	0.29	46	54
triphenylethylene	1.328	33830	33500[*30*]	— 170	— 500	0.92	0.57	0.48	45 30 40	39
methyl-triphenylethylene	1.439	36650	36400[*28*]	+2650	+2400	0.73	0.39	0.38	30 60 60	53
tetraphenylethylene	1.228	31280	32390[*30*]	—2720	—1610	1.08	0.52	0.57	43	48
1,1-diphenylethylene	1.508	40320	40320[*31*]	—	—	0.54	0.27	0.27	34	49
2-methyl-1,1-diphenylethylene	1.558	41600	40320[*23*]	+1280	0	0.52	0.25	0.26	60 30	51
2,2-dimethyl-1,1-diphenylethylene	1.655	44190	40320[*31*]	+3870	0	0.34	0.20	0.17	60	53

a: our results
b: recalculated Suzuki's results

Literature

[*1*] Adrian, F. J.: J. chem. Physics **28**, 608 (1958).
[*2*] Bartell, L. S.: Tetrahedron **17**, 177 (1962).
[*3*] Bastiansen, O.: Acta chem. scand. **4**, 926 (1950).

[*4*] Coulson, C. A.: Proc. Roy. Soc. (London) **A 169**, 413 (1939).
[*5*] — Theoretical Organic Chemistry, p. 49. London: Butterworths Sci. Publ. 1958.
[*6*] Cram, D. J.: J. Amer. chem. Soc. **71**, 3883 (1949).
[*7*] Dahr, J.: Proc. nat. Inst. Sci. India **B 15**, 11 (1949).
[*8*] DeLos, F., DeTar and L. A. Carpino: J. Amer. chem. Soc. **78**, 477 (1956).
[*9*] Dostrovsky, I., E. D. Hughes and C. K. Ingold: J. chem. Soc. **1946**, 173.
[*10*] Gray, G. W.: Steric effects in conjugated systems, p. 62. London: Butterworths Sci. Publ. (1958).
[*11*] Heilbronner, E., and R. Gerdil: Helv. chim. Acta **39**, 1996 (1956).
[*12*] Hendrickson, J. B.: J. Amer. chem. Soc. **83**, 4537 (1961).
[*13*] Hill, T. L.: J. chem. Physics **16**, 938 (1948).
[*14*] Kistiakowsky, G. B., and W. R. Smith: J. Amer. chem. Soc. **56**, 638 (1934).
[*15*] Kitaygorodsky, A. I.: Tetrahedron **14**, 230 (1961).
[*16*] Jaffe, H. H., and M. Orchin: J. chem. Soc. **1960**, 1078.
[*17*] Mixer, R. Y., R. F. Heck, S. Winstein and W. G. Young: J. Amer. chem. Soc. **75**, 4094 (1953).
[*18*] Mulliken, R. S., C. A. Rieke and W. G. Brown: J. Amer. chem. Soc. **63**, 41 (1941).
[*19*] — — Rept. Progr. in Physics 8, 231 (1941).
[*20*] Newman, M. S.: Steric effects in Organic Chemistry, Cap. XII. New York: John Wiley and Sons 1956.
[*21*] Pauling, L.: The nature of the chemical bond, p. 260. Ithaca: Cornell Univ. Press 1960.
[*22*] Pitzer, K. S., L. Guttman and E. F. Westrum Jr.: J. Amer. chem. Soc. **68**, 2209 (1946).
[*23*] Ramart-Lucas, and P. Amagat: Bull. Soc. chim. France (4), **51**, 108 (1932).
[*24*] Robertson, J. M., and I. Woodward: Proc. Roy. Soc. (London) **A 162**, 568 (1937).
[*25*] Schwartzman, L. H., and B. B. Corson: J. Amer. chem. Soc. **78**, 322 (1956).
[*26*] Snyder, L. C.: J. Amer. chem. Soc. **84**, 340 (1962).
[*27*] Streitwieser, A.: Molecular Orbital Theory for Organic Chemists. New York: John Wiley and Sons 1961.
[*28*] Suzuki, H.: Bull. chem. Soc. Japan **25**, 145 (1952).
[*29*] — Bull. chem. Soc. Japan **33**, 379 (1960).
[*30*] — Bull. chem. Soc. Japan **33**, 389 (1960).
[*31*] — Bull. chem. Soc. Japan **33**, 619 (1960).
[*32*] Wilson, E. B.: J. chem. Physics **7**, 1047 (1939).
[*33*] —, and Wells, A. J.: J. chem. Physics **9**, 319 (1941).
[*34*] Wilson, E. B. Jr.: Tetrahedron **17**, 191 (1962).
[*35*] A.P.I.-Research Project 44, p. 483. Pittsburgh: Carnegie Press 1953.

(Received April 11, 1963)