

Figure 1. He(I α) photoelectron spectra of 1,4-divinylbenzene (1) and of 2-phenylbutadiene (2).

correlation between the observed ionization energies $I^m(\pi)$ and the corresponding orbital energies, $\epsilon^{\text{STO-3G}}$ (Table I), calculated for the planar systems. Previous investigations have confirmed the validity of the ab initio STO-3G model as a reliable tool in the interpretation of the photoelectron spectra of unsaturated²² and saturated²³ hydrocarbons. If the conformations of **1** and **2** were grossly at variance with the presumed geometries, such pleasing agreement between theory and experiment would not be expected. Thus, we are led to the conclusion that even the photoelectron spectra of two "isospectral" molecules differ at least as much as those of any pair of molecules for which the representative graphs are of same order (i.e., number of vertices) but not isospectral.

Finally, this result, which relates to an optimal example of chemical interest, strongly suggests that the graph theoretical statement that two molecules are "isospectral" is of no relevance for their physical and chemical behavior.

Acknowledgment. We thank Dr. M. Heitzmann for performing the acetate pyrolysis. T.B.J. thanks the Schweizerischer Nationalfonds for an International Postdoctoral Fellowship. Financial support by Ciba-Geigy SA, by F. Hoffmann-La Roche & Cie. SA, and by Sandoz SA is gratefully acknowledged.

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Received May 2, 1978

Molecular Structure of Pentaphenylethane by X-ray Diffraction

Sir:

Strong interactions between the phenyl rings are expected to occur in pentaphenylethane (PPE). To evaluate the degree of deformation in the molecular framework and the preferred conformation of PPE, we have determined the geometry of this highly strained molecule by X-ray diffraction. Samples of the substance were kindly supplied by Professor G. Olah.

Crystals obtained by fast evaporation of the solvent from a solution of PPE in THF belong to space group $P2_1$, with eight molecules in the unit cell (structure **1**). Of the four molecules in the asymmetric unit, two (molecules A) are ordered and related to each other by a pseudocenter of symmetry, while the other two (molecules B) are randomly disordered. The crystal structure consists of layers of molecules A (each layer being two molecules thick) adjacent to layers of molecules B. The stacking of the layers occurs along c^* , with two different layers in the repeat unit.

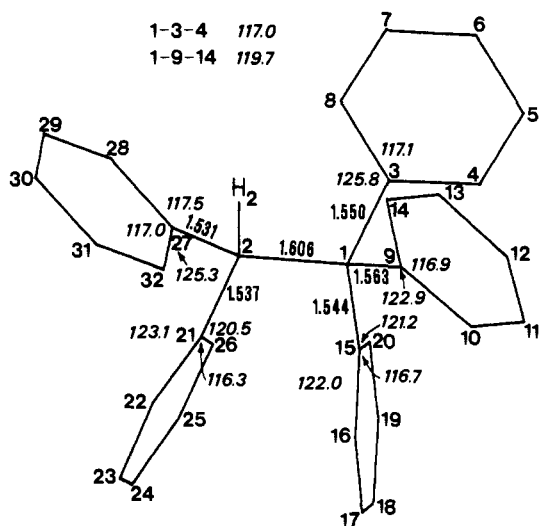


Figure 1. The molecule of PPE viewed down the a axis. Some geometric parameters of interest are reported. esd's are ≤ 0.003 Å for bond distances and $\leq 0.2^\circ$ for bond angles quoted in the figure.

In an attempt to obtain crystals more suitable for an accurate determination of the PPE geometry, a saturated solution of PPE in THF was allowed to slowly evaporate at -30°C . Cell volume, density measurements, and NMR spectra of the derived crystals indicated them to be pentaphenylethane-tetrahydrofuran solvate, with a PPE-THF ratio of 2:1 (structure **2**). Crystal data at room temperature are as follows: $a = 8.677$ (1), $b = 16.633$ (1), $c = 17.037$ (1) Å; $\beta = 95.69$ (2) $^\circ$; $U = 2446.6$ Å 3 ; monoclinic, space group $P2_1/c$; $\mu(\text{Cu K}\alpha) = 5.34$ cm $^{-1}$; $\rho_{\text{measd}} = 1.201$, ρ_{calcd} (assuming four molecules of PPE and two molecules of THF in the cell) = 1.212 g cm $^{-3}$. Intensity data were measured with a Syntex P1 diffractometer using graphite-monochromated Cu K α radiation ($\lambda = 1.5418$ Å). Of the 4088 independent reflections collected within a ϑ sphere of 65° , a total of 3849 with net counts greater than zero were judged observed after usual corrections. The structure was solved by direct methods (MULTAN)¹ and refined assuming a rigid model for the disordered THF,² anisotropic carbon, and isotropic hydrogen atoms. The final value of both R and R_w indices³ is 0.073. Full details of the structure determination and refinement, together with those of the above-mentioned nonsolvate structure **1**, will be published later.

A projection of the PPE molecule down the a axis is shown in Figure 1, where the numbering scheme and some of the geometric parameters are also reported. Values of the bond angles involving the two central atoms C(1) and C(2) are listed in Table I. The degree of deformation of the molecule is well documented by the marked deviations of some bond distances and angles from their standard values. Of particular relevance are the lengthening of the central C(1)-C(2) bond (r_c) to a value as high as 1.606 Å (and, to a lesser extent, that of the C(1)-C(9) bond, 1.563 Å); the closure of the C(3)-C(1)-C(9) bond angle to 102.2° and the expansion of C(1)-C(2)-C(27) to 118.6° ; and the deformation of the two rings at their centers of attachment to the ethane carbon atoms, as shown by the values of the C(1)-C(3)-C(8) and C(2)-C(27)-C(32) angles, 125.8 and 125.3° , respectively.

As expected for a very crowded molecule, there are several short intramolecular contacts, far below the sum of van der Waals radii. They include C(10)⋯C(16), 3.034 Å; C(16)⋯C(21), 3.063 Å; C(4)⋯C(20), 3.076 Å; C(8)⋯C(27), 3.096 Å; C(16)⋯H(10), 2.44 Å; C(3)⋯H(20), 2.49 Å. Small deformations in the ring including atom C(9) result in out-of-plane displacements of 0.018 Å, more than six times the esd; the other four phenyl systems are planar within experimental

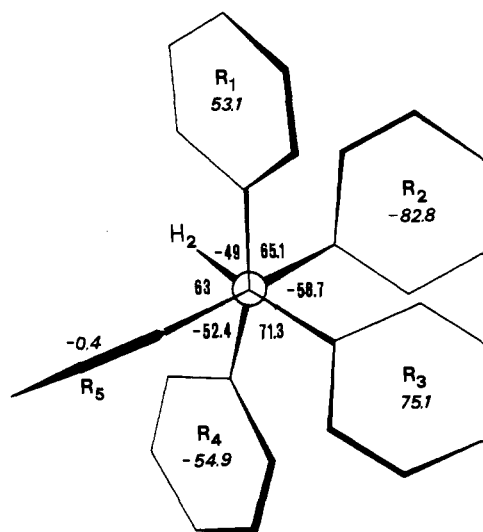


Figure 2. Projection of PPE molecule down the C(1)-C(2) bond. Torsional angles about this bond and rotational angles (in italics) of phenyl rings are reported.

Table I. Bond Angles Involving the Ethane Atoms C(1) and C(2)

angle	deg	angle	deg
C(2)-C(1)-C(3)	114.0 (2)	C(1)-C(2)-C(21)	113.4 (2)
C(2)-C(1)-C(9)	107.6 (2)	C(1)-C(2)-C(27)	118.6 (2)
C(2)-C(1)-C(15)	109.4 (2)	C(21)-C(2)-C(27)	109.2 (2)
C(3)-C(1)-C(9)	102.2 (2)	C(1)-C(2)-H(2)	103 (1)
C(3)-C(1)-C(15)	110.1 (2)	C(21)-C(2)-H(2)	106 (1)
C(9)-C(1)-C(15)	113.6 (2)	C(27)-C(2)-H(2)	105 (1)

uncertainty. There are no particularly short contacts between molecules of PPE at equivalent positions, the shortest distances being C(29)⋯C'(10), 3.564 Å, and C(29)⋯H'(10), 2.70 Å. Similar values occur for the shortest C⋯C and C⋯H contacts between PPE and THF atoms, 3.433 and 2.81 Å, respectively.

Following a previously reported notation,⁴ the conformation of the molecule may be conveniently described by the angles of torsion about the ethane central bond, φ_c , and by those of rotation of the individual phenyl rings, φ_r . Their values are reported in Figure 2, which shows that the molecule of PPE in this crystal structure **2** is nearly staggered. It is worthwhile noting that the conformation of the ordered molecules **A** in the nonsolvate structure **1** is even closer to staggered, the $|\varphi_c|$ values being in the range 60 – 66° . On the contrary, the phenyl systems are differently rotated in the two structures, the φ_r values for rings R₁ to R₅ of structure **1** being -14 , 23 , -51 , -89 , and -73° , respectively. These experimental findings indicate that the staggered conformation of the ethane skeleton can be confidently assumed to be an intrinsic structural feature of PPE, while different packing requirements affect only the external conformation, i.e., the angles of rotation of the phenyl rings.

The molecular conformation and the central bond length r_c of PPE have recently been calculated by the empirical force-field approach.⁴ An input structure with $r_c = 1.56$ Å, $\varphi_c = 60^\circ$, and $\varphi_r = 45^\circ$ was minimized to a nonhelical ground state with individual φ_c values (in the order R₁-R₂, R₂-R₃, . . . , H₂-R₁) of 77.4 , -41.0 , 99.6 , -30.0 , 76.5 , -35.5° .⁵ Two calculated values for r_c were reported, 1.595 Å for the ground state and 1.601 Å for a helical form with a strain energy of 6.5 kcal/mol relative to that of the nonhelical structure. While the values of r_c , particularly the latter, agree well with that obtained by X-ray analysis, the comparison of the φ_c 's yields differences ranging from 12.3 to 28.3° (average difference 18°).

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- For a more favorable comparison with the X-ray results, the enantiomer of the structure calculated by the EFF method⁴ has been considered.

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Received April 5, 1978

Stereoselective Addition of Singlet Oxygen to 7-Isopropylidenenorbornene Derivatives. Possibility of π -Orbital Distortion in the Homoconjugated System¹

Sir:

Because of its relationship to 7-norbornenyl cation,² anion,³ radical,⁴ and 7-norbornenyldiene,⁵ 7-alkylidenenorbornene has received considerable attention. Heilbronner and Martin reported the photoelectron spectrum of 7-isopropylidenenorbornene and estimated the value of orbital splitting due to interaction between the exocyclic double bond and the C₂-C₃ double bond.⁶ Recently Hoffmann and Kurz observed polarization of the exocyclic double bond by measurement of ¹³C NMR spectrum of 7-methylenenorbornene⁷ and established that homoconjugation induces the polarization. It is also anticipated that homoconjugation will induce a distortion of the π orbital of the exocyclic double bond, so that the two sides of the exocyclic double bond will have unequal electron densities. We considered that this distortion could be revealed by chemical reactions, if the following conditions could be satisfied: (1) the chemical reaction should be sufficiently exothermic so that, according to the Hammond postulate,⁸ the transition-state structure would resemble that of the reactant; (2) the reagent should attack only the exocyclic double bond, but not the double bond in norbornene. For these reasons, singlet oxygen⁹ was chosen as a reagent, and the reactions with 7-isopropylidenenorbornene (**1**),¹⁰ the benzo derivative (**2**),¹¹ and the dimethoxycarbonyl derivative (**3**)¹² were investigated.

When a solution of **1**, **2**, or **3** in acetonitrile was photooxidized by irradiation with a 500-W tungsten-Brom lamp in the

Scheme I

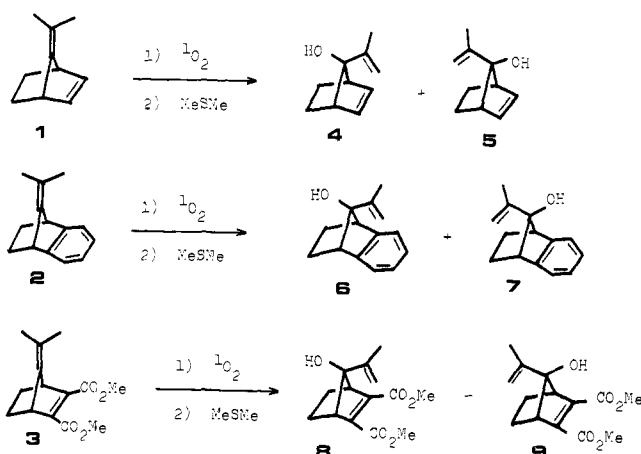
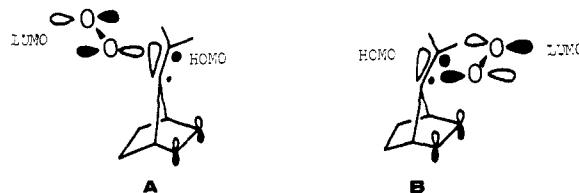


Table I. Yields and Properties of the Products

starting compd	rxn time min	product (% yield; mp, °C)		product, chem shift (δ) of H _{5-exo}	
		anti	syn	anti	syn
1	15	4 (76; ^a oil)	5 (16; ^a 52-54)	4, 2.06 (m) ^c	5, 1.77 (m) ^c
2	20	6 (59; ^a 129-130)	7 (21; ^a 81-83)	6, 2.31 (m) ^d	7, 1.99 (m) ^d
3	120	8 (49; ^b 74-76)	9 (41; ^b oil)	8, 2.22 (m) ^c	9, 1.90 (m) ^c

^a Determined by NMR. ^b Isolated yield. ^c Measured in CCl₄. ^d Measured in CDCl₃.

presence of methylene blue as a sensitizer, followed by reduction with dimethyl sulfide¹³ in methanol, a pair of anti (**4**, **6**, and **8**) and syn (**5**, **7**, and **9**) alcohols was obtained (Scheme I). The yields and properties of the products are shown in Table I, along with the reaction conditions. The stereochemistries of **4**, **5**, **6**, and **7** were assigned by use of the NMR shift reagent, Eu(fod)₃. In addition, as shown in Table I, the chemical shift of the H_{5-exo} protons in all of the syn alcohols appear upfield with respect to the H_{5-exo} in the anti alcohols,¹⁴ because of anisotropic effect of the isopropenyl group. It is of interest to note that the product ratio of the anti to syn alcohols increases in the sequence of **3**, **2**, and **1**. Steric effects of the substituents attached to the C₂ and C₃ carbon, or of the H_{5-exo} protons, do not provide a rationalization for the observed stereoselectivity. A priori, this observation may be explicable by one or more of following factors. (1) The exocyclic double bond bends toward the C₂-C₃ double bond with variation of the angle $\angle C_7C_1C_2$, to increase through-space interaction. (2) The attacking molecular oxygen would experience antibonding interaction with the C₂-C₃ double bond on the syn side.¹⁵ (3) The π orbital of the exocyclic double bond distorts to the anti side by mixing in a σ orbital at the 7 position owing to the perturbation caused by the C₂-C₃ double bond. Concomitantly the geometry of the exocyclic double bond may change owing to hybrid deviation, sp² \rightarrow sp^{2+ α} .¹⁶ We could conclude that factor 1 is not important, because Heilbronner found a small value of IP_{v,2} - IP_{v,1} (0.5 eV) by measurement of the photoelectron spectrum for **1**.⁶ To differentiate between the other two factors, ¹³C NMR spectra of **1**, **2**, and **3** were measured (carbon chemical shifts, δ , at the C₇ and C₈: **1**, 148.6, 106.9; **2**, 148.6, 110.9; **3**, 143.9, 111.9).^{7,17-19} The larger the polarization (Δ , C₇ - C₈: **1**, 41.7; **2**, 37.7; **3**, 32.0), the more the product ratio, anti to syn, increases. The correlation with ¹³C NMR spectra would seem to indicate that factor 3 is more important than factor 2, although factor 2 is not excluded completely. It is possible that stereoselectivity arises from the orbital distortion resulting from the mixing of the π_7^* and σ_7 orbitals.²⁰ Thus, the HOMO represented by $\pi_7 - a\pi_2 - b\pi_7^* + c\sigma_7$ is distorted to the anti side, where mixing coefficients b and c will increase as the coefficient a increases (Figure 1). Orbital interactions in the perepoxide-like transition state are depicted in A and B.



Similar stereoselectivity was also observed in the case of crossed longicyclic compounds²¹ **10** and **11**. After the reduction of the oxidative products of **10**, alcohol **12**,^{22,23} in which the hydroxyl group is anti to the double bond, was produced in better yield (53%) than syn alcohol **13**^{22,23} (33%) (Scheme II).