

- (13) Cf., e.g., F. Gerson, J. Heinzer, H. Bock, H. Alt, und H. Seidl, *Helv. Chim. Acta*, **51**, 707 (1968), or F. Gerson, U. Krynitz, and H. Bock, *ibid.*, **52**, 2512 (1969).
- (14) F. Gerson, U. Krynitz, and H. Bock, *Angew. Chem.*, **81**, 786 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 767 (1969).
- (15) The HMO parameters have been deduced from the photoelectron spectrum:  $\alpha_P = -8.5$ ,  $\alpha_{C(1,4)} = -6.3$ ,  $\alpha_C = -6.15$ ,  $\beta_{PC} = -0.8$ ,  $\beta_{CC} = -3.1$  eV. The ionization potentials calculated with this set—8.16, 8.52, 9.25, and 9.71 eV—agree reasonably well with the experimental values (cf. Table I).
- (16) The parameter  $|Q| = 2.4$  mT (cf. F. Gerson, "High-resolution ESR Spectroscopy", Verlag Chemie, Weinheim/Bertstr., 1970) is probably smaller for radical trianions.
- (17) The hyperfine coupling of the alkali cations is not observed and must be smaller than 0.002 mT.

W. Kaim, H. Bock\*

Institute of Inorganic Chemistry  
University of Frankfurt, Frankfurt, Germany

Received February 8, 1978

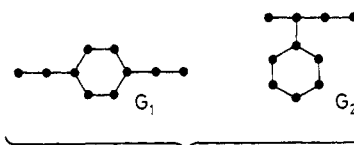
## Spectral Differences between "Isospectral" Molecules<sup>1</sup>

Sir:

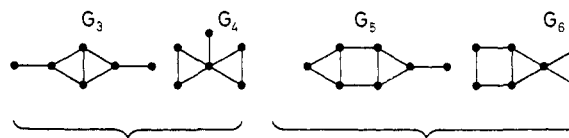
The past few years have witnessed a considerable increase in the number of papers concerning applications of graph theoretical methods<sup>2a</sup> to chemistry.<sup>2b,c</sup> As in other fields, major achievements have been a more transparent description of sequential processes (e.g., configurational<sup>3</sup> and/or conformational<sup>4</sup> changes), efficient methods for computer-assisted storage of structural information,<sup>5</sup> and useful shorthand notations for involved mathematical formulae (e.g., in many-electron treatments<sup>6</sup>). In contrast, the numerous applications of graph theory to simple Hückel-type independent electron models<sup>7</sup> have experienced (in our opinion) only moderate success, inasmuch as they have mainly led to more elegant and mathematically pleasing re-formulations of known results. All of these applications rely in the final analysis on a fundamental observation, due to Günthard and Primas,<sup>8</sup> that such models are purely topological in nature and are thus completely defined by simple, connected graphs  $G$  and their adjacency matrices  $A = A(G)$ . Note that the latter are only defined up to a similarity transformation  $A \sim PAP^T$ , where  $P$  is any permutation matrix. In particular the set  $\{x_j\}$  of the eigenvalues obtained by solving  $\det(A - xI) = 0$ ; i.e., the so-called "spectrum" of the graph  $G$ <sup>9</sup> is postulated to yield the orbital energies  $\epsilon_j = \alpha + \beta x_j$  of such models.<sup>10</sup>

One of the few novel concepts to emerge from graph theory, when applied to molecular orbital theory, is the existence of "isospectral" molecules. Whereas  $\{x_j\} \neq \{x'_j\}$  necessarily implies that the underlying graphs  $G$  and  $G'$  are not isomorphic,  $G \neq G'$ , surprisingly, the converse is not true. As late as 1957 Collatz and Sinogowitz<sup>9</sup> discovered that two nonisomorphic graphs  $G \neq G'$  can indeed have the same spectrum  $\{x_j\} \equiv \{x'_j\}$ , notwithstanding the fact that  $A' \neq PAP^T$  for all possible permutation matrices  $P$ . Such graphs are called "isospectral" and a classical example is provided by the pair  $G_1$  and  $G_2$ :  $\{x_j\} \equiv \{\pm 2.214; \pm 1.675; \pm 1.000; \pm 1.000; \pm 0.539\}$ .

Molecular systems which can be associated with such graphs via a Hückel-type model, e.g., 1,4-divinylbenzene (**1**) with  $G_1$ , 2-phenylbutadiene (**2**) with  $G_2$ , are called "isospectral molecules".<sup>7,11</sup> Obviously  $G_1$  and  $G_2$  are meant to refer only to their  $\pi$  system.



Apart from  $G_1$  and  $G_2$  many other pairs of isospectral graphs have been described in the literature,<sup>12</sup> many of which are, however, unconnected and thus hardly relevant for chemistry. Even pairs of connected isospectral graphs, e.g.,  $G_3$ ,  $G_4$  or  $G_5$ ,  $G_6$ , will not have real molecules as counterparts, for which an independent electron model would give rise to adjacency matrices corresponding to such graphs.



The fundamental, admittedly pragmatic question is whether pairs of "isospectral" molecules, e.g., **1** and **2**, possess measurable physicochemical properties which reflect their "isospectricity". Clearly, a direct measurement of their  $\pi$ -ionization energies by photoelectron spectroscopy is the method of choice<sup>12e</sup> to answer such a question, since all other properties depend to a much lesser degree on purely topological features of the molecular system. For this reason we have recorded the photoelectron spectra of mass- and NMR-pure samples of **1**<sup>13</sup> and **2**,<sup>14</sup> which are presented in Figure 1. In Table I are collected the observed ionization energies  $I_j^m$  (= positions of the band maxima) together with the ionization energies calculated by the SPINDO<sup>15</sup> and ab initio STO-3G models,<sup>16</sup> assuming planar  $\pi$  systems and standard geometries.<sup>17</sup>

It is at once obvious that the photoelectron spectra of **1** and **2** differ at least as much as those of any other "nonisospectral" pair having  $\pi$  systems of comparable size, e.g., naphthalene<sup>18</sup> or azulene,<sup>19</sup> except for the more pronounced vibrational fine structure observed in the latter cases resulting from increased rigidity of the molecules.

It is important to realize that the difference between the two spectra shown in Figure 1 is not due to conformational changes. Thus, on the basis of previous experience<sup>20</sup> both the  $C_{2h}$  and  $C_{2v}$  conformations of **1** will lead to identical  $\pi$ -band systems. Furthermore, slight deviations from coplanarity of the order  $\varphi \leq 20^\circ$  (for the vinyl/phenylene twist angle in **2**), suggested by force-field calculations and by the conformational analysis of 1,3-butadiene or stilbene,<sup>21</sup> cause only insignificant shifts of the band positions ( $\sim 0.1$ – $0.2$  eV). Support for the absence of major deviations from planarity can be found in the excellent

Table I. Observed ( $I_j^m$ ) and Calculated Ionization Energies for 1,4-Divinylbenzene (**1**) and 2-Phenylbutadiene (**2**)<sup>a</sup>

$j$	<b>2</b>					<b>1</b>				
	$I_j^m$	$-\epsilon_j^{\text{STO-3G}}$	$I_j^{\text{calcd}b}$	$-\epsilon_j^{\text{SPINDO}}$	orbital	$I_j^m$	$-\epsilon_j^{\text{STO-3G}}$	$I_j^{\text{calcd}b}$	$-\epsilon_j^{\text{SPINDO}}$	orbital
1	8.60	6.34	8.43	8.77	5a'' $\pi$	8.11	6.00	8.21	8.58	3b <sub>g</sub> $\pi$
2	9.28	7.54	9.21	9.34	4a'' $\pi$	9.18	7.61	9.26	9.34	2b <sub>g</sub> $\pi$
3	9.5	8.03	9.54	9.73	3a'' $\pi$	9.80	8.57	9.89	10.14	2a <sub>u</sub> $\pi$
4	11.2	9.26		10.26	20a' $\sigma$	11.0	10.54	11.18	11.14	1b <sub>g</sub> $\pi$
5	11.54	10.83	11.73	11.39	2a'' $\pi$	11.46	11.50		11.57	10a <sub>g</sub> $\sigma$
6		11.63		11.78	19a' $\sigma$	12.19	11.54		11.91	9a <sub>g</sub> $\sigma$
7		12.41		12.30	18a' $\sigma$		12.38		12.00	10b <sub>u</sub> $\sigma$
8		12.89		12.64	1a'' $\sigma$		12.92		12.68	1a <sub>u</sub> $\pi$

<sup>a</sup>All values are in electronvolts. <sup>b</sup> $I_j^{\text{calcd}}$  from linear regression  $-\epsilon_j^{\text{STO-3G}} = 1.53 I_j^m(\pi) - 6.56$  (correlation coefficient  $r = 0.991$ ).

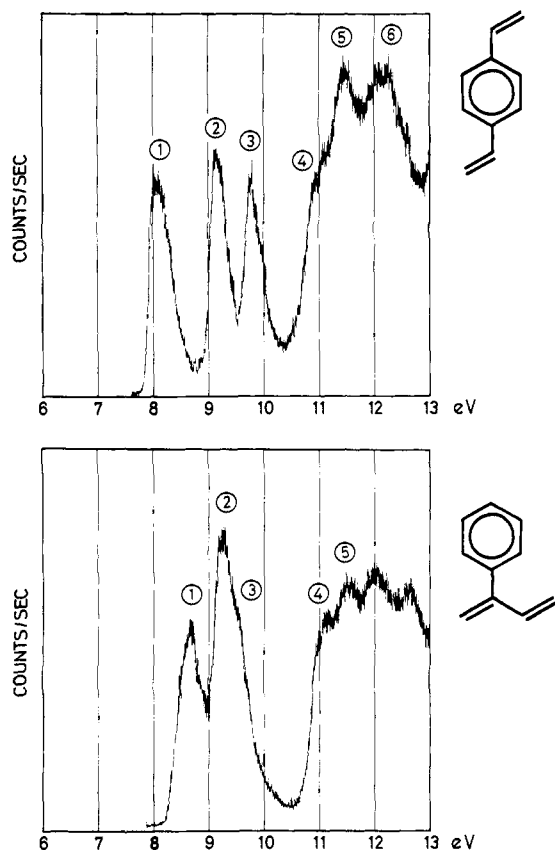


Figure 1. He(I $\alpha$ ) photoelectron spectra of 1,4-divinylbenzene (1) and of 2-phenylbutadiene (2).

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 unsaturated<sup>22</sup> and saturated<sup>23</sup> 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.

## References and Notes

- (1) This work is part 117 of project no. 2.759-0.77 of the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung. Part 116: F. Bieri, F. Brogli, E. Heilbronner, Eise Kloster-Jensen, and J. P. Maier, *Chem. Phys.*, in press.
- (2) (a) F. Harary, "Graph Theory", Addison-Wesley, Reading, Mass., 1969; N. Biggs, "Algebraic Graph Theory", Cambridge University Press, New York, N.Y., 1974. (b) A. T. Balaban, Ed., "Chemical Applications of Graph Theory", Academic Press, London, 1976. (c) D. H. Rouvray, *RIC Rev.*, **4**, 173 (1971).
- (3) E. L. Muetterties, *J. Am. Chem. Soc.*, **90**, 5097 (1968); J. D. Dunitz and V. Prelog, *Angew. Chem.*, **80**, 700 (1968); M. Glielen, *Med. Vlaamse Chem. Ver.*, **31**, 185, 201 (1969); for further references see ref 2b.
- (4) J. Dugundji, P. Gillespie, D. Marquarding, I. Ugl, and F. Ramirez in ref 2b, p 107.
- (5) R. H. Penny, *J. Chem. Doc.*, **5**, 113 (1965); E. Meyer, *Angew. Chem.*, **82**, 605 (1970); A. T. Balaban in ref 2b, p 36; L. J. O'Korn, *ACS Symp. Ser.*, No. **46**, (1977).
- (6) M. A. Robb in "Computational Techniques in Quantum Chemistry and Molecular Physics", G. H. F. Diercksen, B. T. Sutcliffe, and A. Veillard, Ed., NATO Advanced Study Institute Series, D. Reidel Publishing Co., Dordrecht, Netherlands, 1975.
- (7) I. Gutman and N. Trinajstić, *Top. Curr. Chem.*, **42**, 49 (1973); A. Graovac, I. Gutman, and N. Trinajstić, "Topological Approach to the Chemistry of Conjugated Molecules", Springer-Verlag, West Berlin, 1977.
- (8) H. H. Günthard and H. Primas, *Helv. Chim. Acta*, **39**, 1645 (1956).
- (9) L. Collatz and U. Sinogowitz, *Abh. Math. Sem. Univ. Hamburg*, **21**, 63 (1957).
- (10) E. Hückel, *Ann. Phys.*, **70**, 204 (1931); **72**, 310 (1931).
- (11) M. Randić, N. Trinajstić and T. Živković, Progress Report, 1973–1974, Theoretical Chemistry Department, Oxford University.
- (12) (a) A. T. Balaban and F. Haray, *J. Chem. Doc.*, **11**, 258 (1971); (b) F. Haray, C. King, A. Mowshowitz, and R. C. Read, *Bull. London Math. Soc.*, **3**, 321 (1971); (c) T. Živković, N. Trinajstić, and M. Randić, *Mol. Phys.*, **30**, 517 (1975); (d) W. C. Herndon, *Tetrahedron Lett.*, 671 (1974); (e) W. C. Herndon and M. L. Ellzey, Jr., *Tetrahedron*, **31**, 99 (1975); (f) M. Randić, N. Trinajstić, and T. Živković, *J. Chem. Soc., Faraday Trans. 2*, **244**, (1976), and references given therein.
- (13) C. F. Hauser, T. W. Brooks, M. L. Miles, M. A. Raymond, and G. B. Butler, *J. Org. Chem.*, **28**, 372 (1963); <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.28 (s, 2 H), 6.63 (d, d, 1 H), 5.63 (d, d, 1 H,  $J_{\text{trans}} = 18$  Hz,  $J_{\text{gem}} = 1$  Hz), 5.15 (d, d, 1 H,  $J_{\text{cis}} = 11$  Hz,  $J_{\text{gem}} = 1$  Hz); mass spectrum  $m/e$  130 ( $M^+$ ,  $B^+$ ).
- (14) C. C. Price, F. L. Benton, and C. J. Schmidle, *J. Am. Chem. Soc.*, **71**, 2860 (1949); <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.25 (m, 5 H), 6.57 (m, 1 H), 5.13 (m, 4 H); mass spectrum  $m/e$  130 ( $M^+$ ,  $B^+$ ).
- (15) L. Asbrink, C. Fridh, and E. Lindholm, *J. Am. Chem. Soc.*, **94**, 5501 (1972); C. Fridh, L. Asbrink, and E. Lindholm, *Chem. Phys. Lett.*, **15**, 282 (1972).
- (16) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, QCPE, Bloomington, Ind.
- (17) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
- (18) P. A. Clark, F. Brogli, and E. Heilbronner, *Helv. Chim. Acta*, **55**, 1415 (1972); R. Boschi, E. Clar, and W. Schmidt, *J. Chem. Phys.*, **60**, 4406 (1974).
- (19) J. H. D. Eland and C. Danby, *Z. Naturforsch. A*, **23**, 335 (1968); E. Heilbronner, T. Hoshi, J. L. von Rosenberg, and K. Hafner, *Nouv. J. Chim.*, **1**, 105 (1977).
- (20) M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *Helv. Chim. Acta*, **56**, 1028 (1973).
- (21) R. L. Lipnick and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **95**, 6370 (1973); M. Traetteberg, E. B. Frantsen, F. C. Mijlhoff, and A. Hoekstra, *J. Mol. Struct.*, **26**, 57 (1975).
- (22) G. Bieri, J. D. Dill, E. Heilbronner, J. P. Maier, and T. Ripoll, *Helv. Chim. Acta*, **60**, 629 (1977); G. Bieri, E. Heilbronner, T. Kobayashi, A. Schmelzer, M. J. Goldstein, R. S. Leight, and M. S. Lipton, *ibid.*, **59**, 2657 (1976); F. Brogli, E. Heilbronner, E. Kloster-Jensen, A. Schmelzer, A. S. Manocha, J. A. Pople, and Leo Radom, *Chem. Phys.*, **4**, 107 (1974).
- (23) P. Bischof, P. E. Eaton, R. Gleiter, E. Heilbronner, T. B. Jones, H. Musso, A. Schmelzer, and R. Stober, *Helv. Chim. Acta*, **61**, 547 (1978); G. Bieri, J. D. Dill, E. Heilbronner, and A. Schmelzer, *ibid.*, **60**, 2234 (1977).

Edgar Heilbronner,\* and Taylor B. Jones

Physikalisch-chemisches Institut der Universität Basel  
CH-4056 Basel, Switzerland

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.