

## ISOSPECTRAL GRAPHS AND MOLECULES

W. C. HERNDON\* and M. L. ELLZEY, JR.

Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968

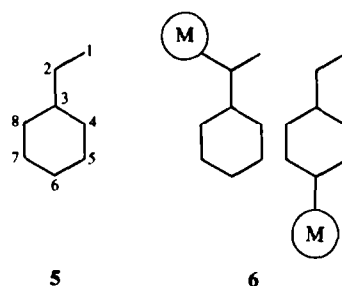
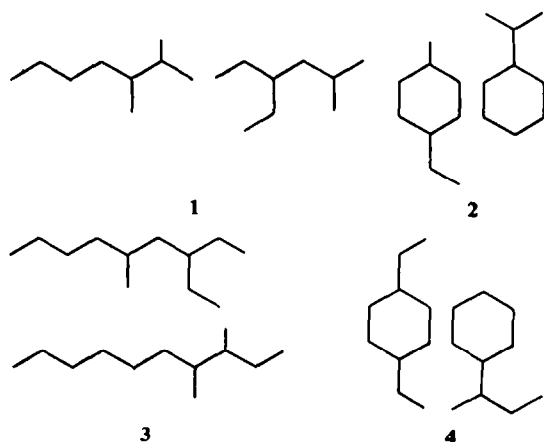
(Received in USA 23 May 1974; Received in the UK for publication 28 August 1974)

**Abstract**—Isospectral molecules are nonidentical species whose molecular graphs have the same set of eigenvalues within HMO calculations. Several new concepts and methods for constructing pairs of isospectral graphs are discussed. Some possible experimental and theoretical applications of isospectral molecular pairs are outlined.

### INTRODUCTION

In recent short papers we discussed the concept of "isospectral" molecules.<sup>1</sup> The term is taken from the literature of graph theory,<sup>2-4</sup> where a graph is defined to have an adjacency (topological<sup>5,6</sup>) matrix, an associated characteristic polynomial, and a set of eigenvalues for the adjacency matrix called the spectrum of the graph. Isospectral graphs are nonidentical graphs whose nonidentical adjacency matrices give identical characteristic polynomials and sets of eigenvalues.<sup>7-11</sup> Conjugated  $\pi$ -systems can be represented by simple graphical figures, and the adjacency matrix of a graph is isomorphic with the HMO secular matrix for the  $\pi$ -system represented by the graph. Therefore one must admit the possibility of isospectral  $\pi$  molecular species, different systems that have identical energy levels.

We gave examples of the smallest pairs of isospectral open-chain and monocyclic hydrocarbon  $\pi$ -systems that are of interest to organic chemists.<sup>1</sup> These are the polyene radicals 1, the aromatic radicals shown in 2, the dodecahexaene isomers 3, and the 1,4-divinylbenzene 2-phenylbutadiene pair given in 4. We also defined the concept of "isospectral points" in the styrene graph, vertices 2 and 6 in 5. Attachment of any moiety M to points 2 and 6 in turn gives two nonisomorphic isomers, shown in 6, whose spectra of eigenvalues are identical.

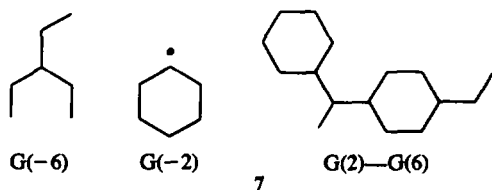


The potential uses of isospectral species have only been alluded to in previous work, and from a rather negative viewpoint. For example, we pointed out<sup>1</sup> that the existence of pairs of isospectral molecules in which one compound is formally cross-conjugated in comparison to the other (e.g., the pairs in 3 and 4) did not support the usual presupposed idea of the general effect of cross-conjugation. Other workers have considered isospectral pairs solely as impediments to designing computer-based chemical reference systems.<sup>12-15</sup>

In the present paper we will try to suggest some positive applications related to experimental consequences of isospectrality. Also, general methods for locating isospectral points and constructing isospectral molecular graphs will be given, along with a description of our mathematical approach. A new structural feature, unrestricted substitution points which maintain the existence of isospectral points, will be described. Finally we will give numerous examples of isospectral molecular pairs simply because we think they are intriguing *per se*, and because we believe their syntheses and correlations of properties with theory provide interesting new challenges in organic chemistry.

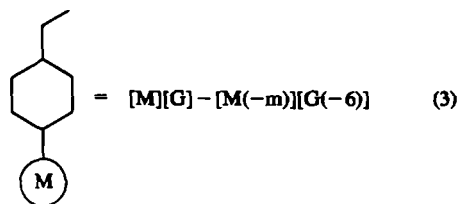
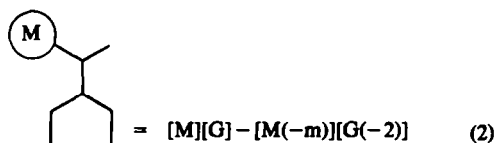
### DEFINITIONS AND PROCEDURES

The graphical figure itself or a capital letter will be used to represent a molecular graph. As an example G could represent the styrene graph in 5. The graph obtained after deletion of a single vertex and connecting edges will be designated as G(-i) where i is the index of the deleted vertex, and the symbol G(r)-G(s) will stand for a connected graph with two components of type G joined at r and s respectively. Examples are given in 7.



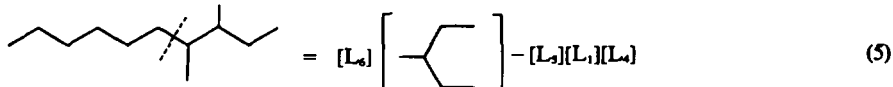
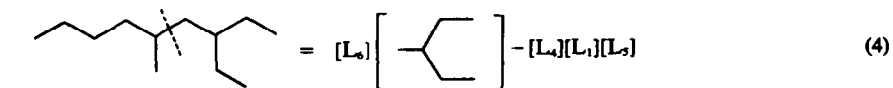
The graph or the alphanumeric designation, usually in brackets, will also be used to stand for the characteristic polynomial of the adjacency matrix of the graph, which for brevity will be called the polynomial of the graph. To demonstrate that two different systems are isospectral we find that it is much easier and faster to show the equivalence of their polynomials than to solve for the eigenvalues of their secular matrices. Also, one should note that it is usually not necessary to write out the terms of the polynomial since an equivalency of graphical symbols rigorously shows an equivalency of associated polynomials.

Our main tools for manipulating the polynomials and



arbitrary graph. Infinite numbers of isospectral graphs are therefore obtainable using this principle.

A proof that the open-chain (tree graphs) pair shown in 3 are isospectral serves to illustrate our methods further. If we let  $L_n$  represent a linear tree graph with  $n$  vertices, scission at the points indicated in Eqs 4 and 5



graphical symbols are decomposition theorems of Heilbronner,<sup>16</sup> and a graphical method for enumeration of the coefficient terms in the secular polynomial due to Coulson<sup>17</sup> and Sachs.<sup>18</sup> Heilbronner showed how the polynomials for complex systems could be derived from those of the component parts, Eq 1. The polynomial for a system

$$[P] = [Q(q) - R(r)] = [Q][R] - [Q(-q)][R(-r)] \quad (1)$$

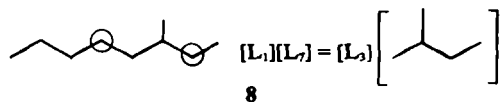
$P$  composed of two parts  $Q$  and  $R$  joined by points  $q$  and  $r$  respectively is equal to the product of the polynomials of the component parts minus the product of the component graphs with the joining points deleted. First we use Heilbronner's method to simplify the graphical figures, and then apply the Coulson-Sachs theorem to find the actual polynomials. We will not describe the Coulson-Sachs method except to say that each coefficient in the secular polynomial is a simple function of the number of ways the graph can be partitioned into disjointed two-point and cyclic graphs. Adequate expository descriptions of the method are available<sup>4,19</sup> and the technique can be learned easily in a few minutes.

As an example, let us compare the polynomials of the two graphs stated to be isospectral in 6. Examination of Eqs 2 and 3 shows that the polynomials are identical if  $G(-2) = G(-6)$ . Their polynomials are respectively  $(X^6 - 6X^4 + 9X^2 - 4)$  and  $(X^7 - 6X^5 + 9X^3 - 4X)$  which are identical after multiplication in the first expression. Incidentally this also demonstrates that points 2 and 6 in the styrene graph are isospectral points since  $M$  is an

and the use of Heilbronner's theorem gives the two sets of identical terms shown. This example also shows that it is not necessary for isospectral graphs to be derivatives of a parent graph with isospectral points. In the case of isospectral graphs 3 there does exist a mutual reciprocal relationship of the structural fragments obtained upon simple scission, but the example given in 1 shows that this also is not a necessary condition for isospectrality. As far as we can discover, one must identify isospectral pairs such as those in 1 by trial and error or serendipity. We will not discuss examples obtained by these latter two methods in this paper.

#### ISOSPECTRAL POINTS AND UNRESTRICTED SUBSTITUTION POINTS

The identification of isospectral points in molecular graphs is a very important aspect of a consideration of the isospectral phenomenon. No discussions exist in the graph theory literature except for a single article by Schwenk<sup>11</sup> concerned with the 9-point graph shown in 8, where the two isospectral



points are circled. In the case of 8 the discovery of the isospectral points was evidently fortuitous, so the work does not provide any sort of guide for future exploration.

In this section we will describe three more or less

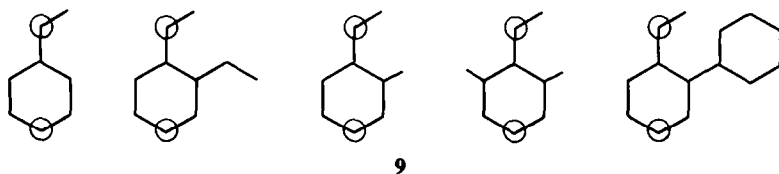
general methods for locating isospectral points and for generating molecular graphs with isospectral points.

**HMO theory.** Vertices in a molecular graph that are related by symmetry are not isospectral. Substitution at such points successively will give two identical graphs rather than two nonisomorphic graphs with identical polynomials. However a consideration of the symmetric points led us to conjecture that isospectral points must have identical absolute values of eigenvectors in every nondegenerate eigenlevel. A proof of this conjecture is given in an appendix, and one can easily see that the hypothesis is true by examining tables of eigenvectors and eigenvalues for particular systems. Many good compilations are available, and several pairs of isospectral points in readily available  $\pi$ -systems can be discovered in this way. Those taken from the Coulson and Streitwieser compilation<sup>20</sup> are circled in 9-17. One notes that a

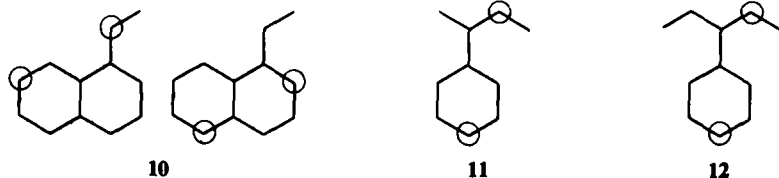
molecule may possess more than one pair of isospectral points as for example in 16, 1-vinylphenanthrene, which has 4 sets.

Isospectral pairs of molecular systems of many different types can be obtained by utilizing these structures. Some general theorems and procedures will be given later. For now, we will just mention that isospectral species can also be obtained either by deletion of isospectral points or by changing the isospectral points to heteroatoms in turn. In the latter case, the change to a heterosystem must be accomplished within the HMO type of accommodation of heteroatoms, i.e., differing Coulomb and nearest neighbor resonance integrals.

**Unrestricted substitution points.** Inspection of the graphs in 9 shows that substitutions of methylene, vinyl, or phenyl groups ortho to the vinyl group of styrene graph do not have any effect on the isospectrality of vertices 2



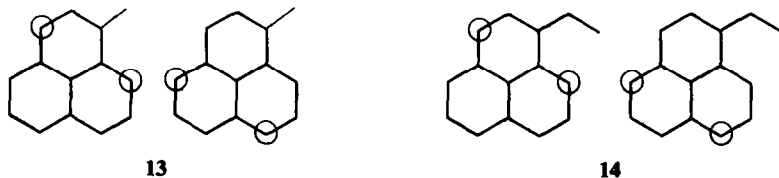
9



10

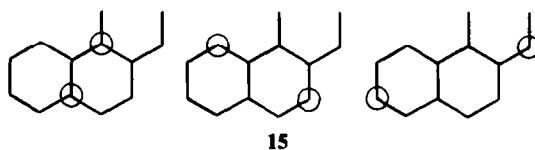
11

12

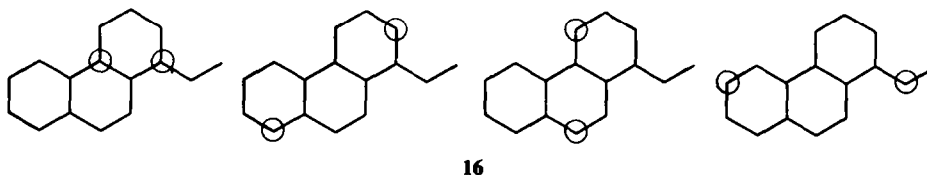


13

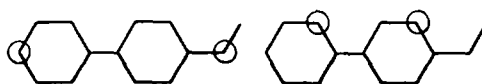
14



15



16

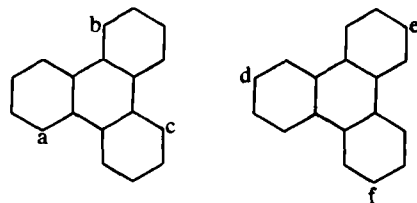


17

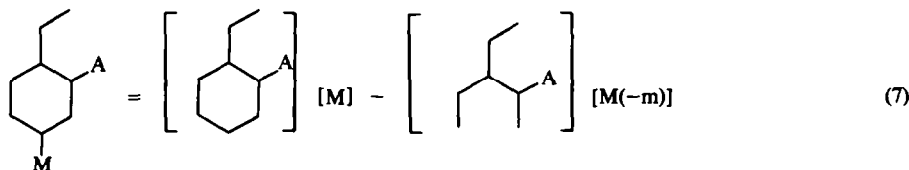
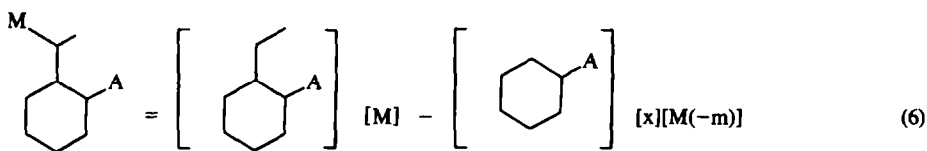
and 6. One may surmise that the ortho positions are unrestricted points where substitution of any kind leaves the original isospectral points invariant from this standpoint. If this is true, and if unrestricted points are generally available, the potential pool of isospectral sets of molecules becomes enormously multiplied. From the styrene graph alone one can obtain any number of isospectral pairs of molecules by substitution first at the ortho position and then substitution in turn at the two isospectral points. The substituents can be of any type and size including hetero and saturated moieties. The proof of the conjecture is easily demonstrated as shown in Eqs 6 and 7, since all terms on the right-hand sides of Eqs 6 and

7 are identical, cf. Eqs 2 and 3 and subsequent discussion. Because of the symmetry, points a, b, and c are equivalent points, as are d, e, and f. The absolute values of their eigenvectors must be identical in nondegenerate eigenlevels. The reciprocal pair-wise perturbations a-b, b-c, c-a are also required to be identical from symmetry, and similarly for the pairs d-e, e-f, and f-d. This means that substitution at a destroys the 3-fold symmetry of the molecular graph but must leave the points b and c isospectral. A substituent may be added at a which is now an unrestricted point for isospectral points b and c. The same considerations hold for the second graph in 21, and examples of the general potential nonisomorphic isospectral pairs of graphs are given in 22.

Incidentally, the ideas discussed in the previous paragraph also reveal another method for finding graphs with isospectral points. Removal of point a or d from triphenylene can be looked upon as a type of substitution. The resulting graphs have isospectral points as shown by

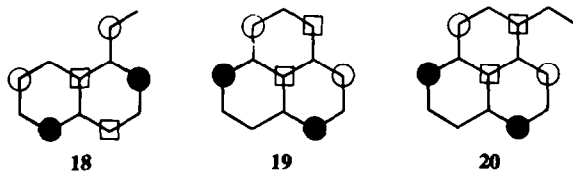


21



7 are identical, cf. Eqs 2 and 3 and subsequent discussion. In the same way, one can also show that simultaneous introduction of two different substituents at both unrestricted positions preserves the isospectral points at positions 2 and 6.

Our experience with HMO theory let us to expect that the Coulson Longuet-Higgins<sup>21</sup> atom-atom polarizabilities of styrene graph ortho positions with either of the two isospectral points ought to be numerically the same. To second-order substitution at unrestricted points would then effect eigenvectors of isospectral points equivalently. The expectation proved to be correct for the styrene graph, implying that one could also use HMO tables to find unrestricted substituent points. Using this approach, in conjunction with the Coulson-Streitwieser tables, unrestricted points were discovered in graphs 10, 13, and 14, as shown by the squares in 18, 19, and 20 respectively.



18

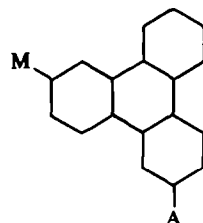
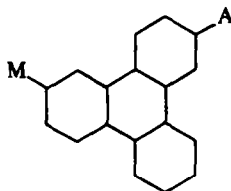
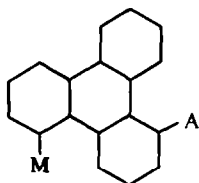
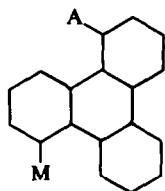
19

20

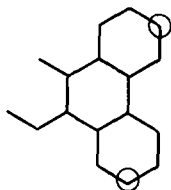
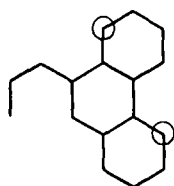
In fact each system has two unrestricted points for both pairs of isospectral points. The graphs in 19 and 20 are actually special cases (in part) of a more general type of system which will always have at least one unrestricted point and an isospectral pair of points. The basic structure is any polycyclic structure with a high order of rotational

symmetry ( $C_n > C_2$ ). Systems with 3-fold symmetry are especially useful and are described in the next subsection. The graph given in 25 shows that isospectrality is not confined to alternant systems.

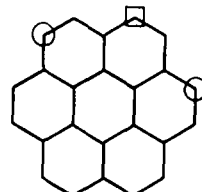
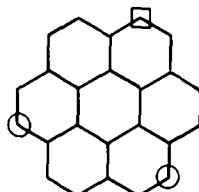
*A decomposition principle.* At present we have found one additional way to generate graphs with isospectral



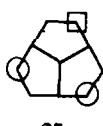
22



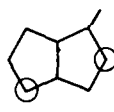
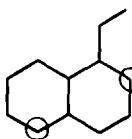
23



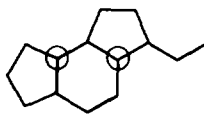
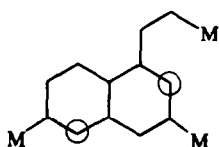
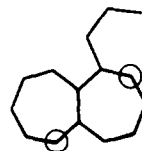
24



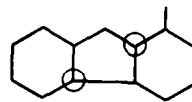
25



26



27



points. In certain molecular graphs there are particular non-equivalent points that seem to be related by a pseudo-symmetric element in that removal first of one point and then the other does generate identical graphs. The circled points in all of the graphs given in 26 are of this type. For example, deletion of either point in 1-vinyl-naphthalene gives rise to 1-propenyl-2-vinylbenzene graph, and a consideration of the Heilbronner decomposition theorem demonstrates the isospectrality of each pair of vertices. One can of course invert the whole thinking process and build any number of graphs with isospectral points if one retains the decomposition structural feature of the graphs in 26. The structures with circled isospectral points shown in 27 were induced in this way. Many hundreds of additional examples could be given, but we hope these few are enough for illustrative purposes.

#### GENERAL PROPERTIES OF ISOSPECTRAL POINTS

In this section, we will state some general theorems regarding substitution properties of isospectral and unrestricted points. The theorems are best understood with the aid of examples, and we will use the styrene

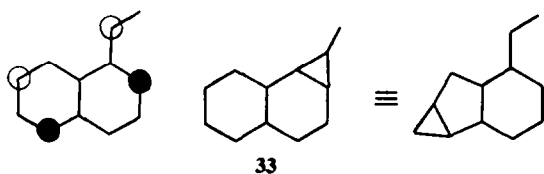
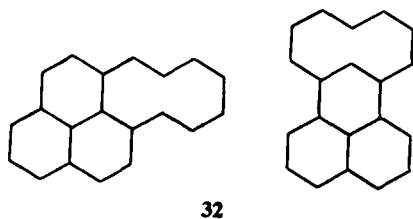
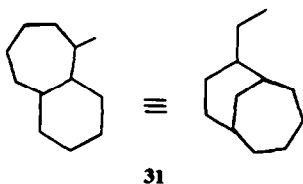
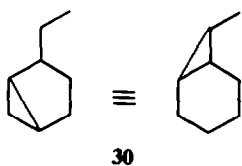
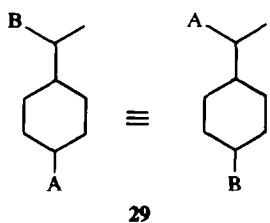
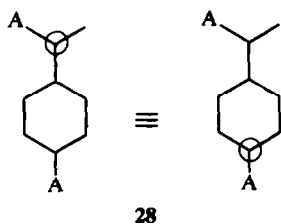
graph to illustrate many of the properties. However, it should be understood that each theorem is perfectly general and applies to all graphs with isospectral points. No mathematical proofs of the theorems will be given, but each one can be easily shown to be true.

*Attachment of identical substituents simultaneously at isospectral points leaves the points isospectral.* Graphs of this type with heteroatoms at the isospectral points are obvious chemically interesting examples.

*Two different substituents attached to two isospectral points in a reciprocal relationship generate isospectral molecular graphs.*

*Attachment of unrestricted points through any moiety to each of a pair of isospectral points in turn generates isospectral species.* Some interesting isospectral annulenes as shown in 32 can be generated using this principle.

*In systems with two or more pairs of isospectral points, the differing sets may be connected through any moiety to yield isospectral species.* We are certain that there are many more extensions and corollaries of these theorems. However, these particular relationships are the only ones that will be used in the subsequent discussion.



#### APPLICATIONS

Isospectral molecular species are nonisomorphic systems with identical sets or spectra of eigenvalues. However, the eigenvalues are only identical within those approximate types of MO calculations that postulate Hamiltonian matrix elements for bonded neighboring atomic positions. Isospectral pairs are therefore obviously useful for distinguishing between those physical and chemical properties that are solely functions of the

bonding topological network, and properties that are functions of longer range interactions. An isospectral pair of molecules could allow one to test the accuracy of a simple MO calculation as compared to some more elaborate type of theoretical approach.

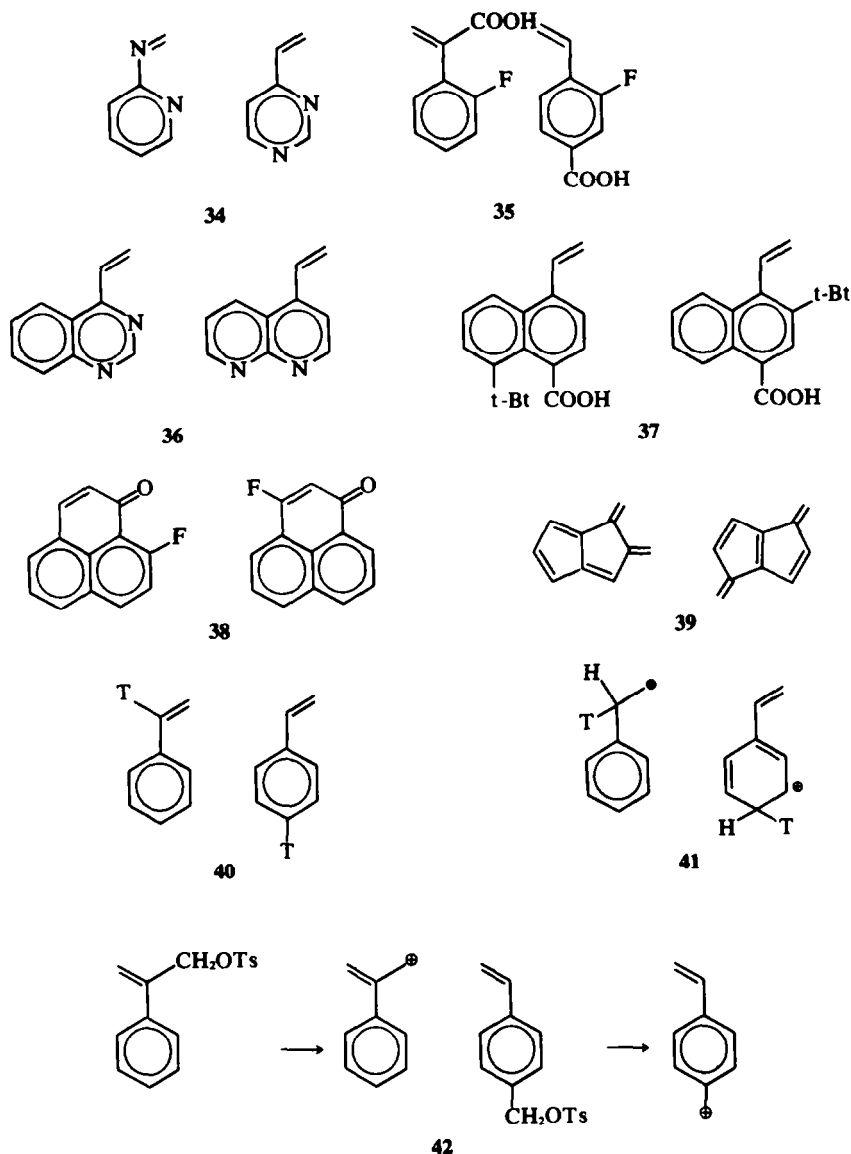
For example, an isospectral pair should have identical oxidation potentials if the HMO method is sufficient to describe the  $\pi$ -systems under consideration. Any differences would have to arise from some factors which are not considered in the HMO approximation. Some of these factors could be nonplanarity, interaction of the  $\sigma$  and  $\pi$  system, variable bond lengths, inductive effects propagated to distant atoms, and field effects transmitted through space. The devising of structural pairs which isolate a single one of these factors will be a fruitful endeavor for future work.

One additional aspect of isospectral and unrestricted points needs some comment. Although we have been careful to use abstract symbols for the substituent moieties, the very general nature of a possible substituent should be emphasized. The substituent at an unrestricted point or isospectral point can be a  $\pi$ -system, an alkyl chain, heteroatoms or chains with heterosubstituents, or even the annihilation substituent, i.e., the deletion of the vertex. The theoretical description of the substituent is immaterial. Any types of parameterization or formulae for matrix elements in the substituent have absolutely no effect on the isospectral qualities being considered. Substituents of any type at unrestricted points leaves the isospectral points, and successive substitution at isospectral points always gives a pair of isospectral molecules.

The eigenvalues from an MO calculation can be correlated with resonance energies, ultraviolet spectra, oxidation and reduction potentials, and certain kinds of reactivity.<sup>22</sup> Assuming Koopmans' postulate<sup>23</sup> photoelectron spectroscopy can provide detailed orbital energy level diagrams for organic molecules,<sup>24</sup> and this is probably the preferred experimental method for comparison of isospectral molecules. The pairs shown in 34-40 are meant to be illustrative of the many different types of pairs of systems that can be constructed.

The ionization constants of the carboxylic acids in 35 might give some insight into fluorine substituent field effects or possibly reflect hydrogen-bonding to fluorine in one of the isomers. If the ionization constants of the acids in 37 differ this could reflect a buttressing effect of the bulky *t*-butyl substituent in the *peri* position. The point is that both unionized acids and the anion isomers are perfectly isospectral. Nonbonded interactions must account for any observed differences.

The diazo compounds 34 should have identical photoelectron spectra. An observed difference could be a function of variable bondlengths or nonplanarity of vinyl and aromatic ring components. Nonidentical spectra for 36 and 39 would not be explainable on those grounds. Lone-pair "*peri*" effects might account for different properties in 36. In 38 one could study the carbonyl stretching frequencies and attribute difference to differing field effects of the fluorine substituents. It would be interesting to study the rates of tritium isotope exchange



in sulfuric acid using the tritium substituted styrene isomers in 40. In this case, both ground state molecules and the carbonium ion intermediates are isospectral even though one carbonium ion is formally more localized than the other.

Gleicher has carried out variable bond-length SCF-LCAO-MO calculations on phenylisopropenyl and 4-vinylbenzyl cations as shown in 42.<sup>25</sup> Within the HMO approximation these cations are of course isospectral and therefore isoenergetic. The SCF calculations give very different results with the isopropenyl system more stable. The relationship between the two systems could be possibly studied by investigating the rates of solvolysis of parent *p*-toluene-sulfonate esters. Gleicher suggests that studies of systems of this type might allow firm

conclusions as to which theoretical method (HMO or SCF) is better for this class of structures.

#### SUMMARY

We have given many detailed examples of our inductive methods for constructing isospectral molecules so that others will be able to construct their own systems of interest. We have also given a few examples of isospectral pairs of molecules that may prove interesting if subjected to experimental study. Finally we made some short comments on possible experiments in which the isospectral pairs could be used to provide information about intramolecular structural interactions in both ground-state molecules and reactive intermediates. We expect many additional developments.

**Acknowledgement**—The financial support of the Robert A. Welch Foundation is gratefully acknowledged. The designation of the term "unrestricted point" is due to the comments of a referee which are also appreciated.

## REFERENCES

- <sup>1</sup>W. C. Herndon, *Tetrahedron Letters* 671 (1974); *J. Chem. Doc.* 14, 150 (1974)
- <sup>2</sup>F. Harary, *Graph Theory*, Addison-Wesley, Reading, Mass. (1969)
- <sup>3</sup>D. H. Rouvray, *R. I. C. Reviews* 4, 173 (1971)
- <sup>4</sup>I. Gutman and N. Trinajstić, *Topics in Current Chem.* 42, 49 (1973)
- <sup>5</sup>N. S. Ham and K. Ruedenberg, *J. Chem. Phys.* 29, 1199 (1958)
- <sup>6</sup>K. Ruedenberg, *Ibid.* 34, 1861 (1961)
- <sup>7</sup>L. Collatz and U. Sinogowitz, *Abh. Math. Sem. Univ. Hamburg* 21, 64 (1957)
- <sup>8</sup>F. Harary, *SIAM Review* 4, 202 (1962)
- <sup>9</sup>F. Harary, C. King, A. Moshowitz and R. C. Read, *Bull. London Math. Soc.* 3, 321 (1971)
- <sup>10</sup>A. Moshowitz, *J. Comb. Theory* 12(B), 177 (1972)
- <sup>11</sup>A. J. Schwenk, *New Directions in the Theory of Graphs*, (Edited by F. Harary) p. 275. Academic Press, New York, N.Y. (1973)
- <sup>12</sup>L. Spaltier, *J. Chem. Doc.* 4, 269 (1964)
- <sup>13</sup>A. T. Balaban and F. Harary, *Ibid.* 11, 258 (1971)
- <sup>14</sup>H. Hosoya, *Ibid.* 12, 181 (1972)
- <sup>15</sup>T. Kudo, T. Yamasaki and S.-I. Sasaki, *Ibid.* 13, 225 (1973)
- <sup>16</sup>E. Heilbronner, *Helv. Chim. Acta* 36, 170 (1953)
- <sup>17</sup>C. A. Coulson, *Proc. Camb. Phil. Soc.* 46, 202 (1949)
- <sup>18</sup>H. Sachs, *Publ. Math. Debrecen* 11, 199 (1963)
- <sup>19</sup>A. Granovac, I. Gutman, N. Trinajstić and T. Zivković, *Theor. Chim. Acta Berlin* 26, 67 (1972)
- <sup>20</sup>C. A. Coulson and A. Streitwieser, Jr., *Dictionary of  $\pi$ -Electron Calculations*. Pergamon Press, New York, N.Y. (1969)
- <sup>21</sup>C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* A191, 39 (1947); A192, 16 (1947); A193, 447 (1948); A195, 188 (1948)
- <sup>22</sup>A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, N.Y. (1961)
- <sup>23</sup>T. Koopmans, *Physica* 1, 104 (1934)
- <sup>24</sup>D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, *Molecular Photoelectron Spectroscopy*. Wiley-Interscience, London (1970)
- <sup>25</sup>G. J. Gleicher, personal communication. We are grateful to Prof. Gleicher for this information
- <sup>26</sup>P. A. M. Dirac, *Quantum Mechanics* 4th Ed., Oxford University Press, Fair Lawn, N.J. (1957)

## APPENDIX

In this appendix we give a theorem which provides a useful means for the identification of isospectral points based upon the coefficients of eigenvectors of a graph. Although this theorem fails to distinguish between isospectral and equivalent points, the latter points can be eliminated by relating them to symmetry operations on the graph. Those unfamiliar with the *bra* and *ket* notations employed here are referred to Dirac.<sup>26</sup>

**Theorem.** Let  $(i|q)$  denote the  $i^{\text{th}}$  component of the  $q^{\text{th}}$  degenerate eigenvector of the weight matrix  $W$  of a graph  $G$  corresponding to an eigenvalue  $E_q$ , where  $l = 1, 2, \dots, L$ , and  $q = 1, 2, \dots, Q_l$ . Points  $i_0$  and  $j_0$  of  $G$  are either isospectral or equivalent if and only if

$$\sum_q^{Q_l} ((i_0|q))^2 = \sum_q^{Q_l} ((j_0|q))^2.$$

**Proof.** We consider the weight matrix  $W_T$  of a graph  $G_T$  constructed by connecting  $m'$  of the points of any graph  $G'$  to the point  $i_0$  of the original graph  $G$ . In this development, primed quantities are to be associated with  $G'$  and unprimed quantities with  $G$ . The form of  $W_T$  is

$$W_T = \begin{bmatrix} W & X \\ X' & W' \end{bmatrix}$$

where  $X$  contains the weights of the connections between  $G$  and  $G'$ . Since these connections are all to point  $i_0$  of  $G$ , the elements of  $X$  have the form

$$\langle i|X|i' \rangle = \delta(i, i_0)w_r.$$

It is convenient to require the eigenvectors of both  $W$  and  $W'$  to be orthonormal. In addition, we assume that degenerate eigenvectors of  $W$  have been selected so that the  $i_0$  component is nonzero for only one vector, say  $q = 1$ , in each degenerate set,

$$\langle i_0|c, lq \rangle = \delta(q, 1)\langle i_0|c, l1 \rangle.$$

The index  $c$  identifies the components associated with such a choice. By orthonormality, these components are related to those in any set by

$$(\langle i_0|c, l1 \rangle)^2 = \sum_{q=1}^{Q_l} (\langle i_0|lq \rangle)^2.$$

On a basis consisting of the eigenvectors of  $W$  followed by the eigenvectors of  $W'$

$$\{|c, l1 \rangle, \dots, |c, lq \rangle, \dots, |c, lQ_l \rangle, |l'1' \rangle, \dots, |l'q' \rangle, \dots, |l'Q'_l \rangle\}$$

$W_T$  is transformed to a partitioned matrix of the type

$$\begin{bmatrix} E & Y \\ Y' & E' \end{bmatrix}$$

where  $E$  and  $E'$  are diagonal matrices containing the eigenvalues of  $W$  and  $W'$ . The elements of the interaction matrix  $Y$  are given by

$$\begin{aligned} \langle c, lq|Y|l'q' \rangle &= \sum_i \sum_{i'} \langle c, lq|i \rangle \langle i|X|i' \rangle \langle i'|l'q' \rangle \\ &= \sum_i \sum_{i'} \delta(i, i_0) \delta(q, 1) \langle c, l1|i_0 \rangle w_r \langle i'|l'q' \rangle \\ &= \delta(q, 1) \langle c, l1|i_0 \rangle \sum_{i'} w_r \langle i'|l'q' \rangle \\ &= \delta(q, 1) \langle c, l1|i_0 \rangle S(l'q'). \end{aligned}$$

Thus the elements of a row of  $Y$  indexed by  $l$  and  $q$  are all zero if  $q \neq 1$ , or contain  $\langle c, l1|i_0 \rangle$  as a factor if  $q = 1$ . Similarly, the elements of a column of  $Y'$  indexed by  $l$  and  $q$  are all zero if  $q \neq 1$ , or contain  $\langle i_0|c, l1 \rangle$  as a factor if  $q = 1$ . In the secular equation

$$\det \begin{bmatrix} E - \lambda I & Y \\ Y' & E' - \lambda I \end{bmatrix} = 0$$

we can divide each row indexed by  $l$  and  $q = 1$  by  $\langle c, l1|i_0 \rangle$  and each column indexed by  $l$  and  $q = 1$  by  $\langle i_0|c, l1 \rangle$  to obtain

$$\det \begin{bmatrix} Z & S \\ S' & E' - \lambda I \end{bmatrix} = 0.$$



The elements of Z are

$$\langle c, l_1 q_1 | Z | c, l_2 q_2 \rangle = \delta(l_1, l_2) \delta(q_1, q_2) \begin{cases} E_l - \lambda & q = 1 \\ (i_0 | c, l_1 \rangle)^2 & q \neq 1 \\ E_l - \lambda & q \neq 1 \end{cases}$$

points and weights  $w_i$  of  $G'$ , the only change in the secular equation occurs in the denominators of the elements of Z. The same eigenvalues of  $W_T$  will therefore be obtained in general only if

$$\langle i_0 | c, l_1 \rangle^2 = \langle j_0 | c, l_1 \rangle^2, \quad l = 1, 2, \dots, L.$$

and the elements of S are

$$\langle c, l q | S | l' q' \rangle = \delta(q, q') S(l, l').$$

Consequently, the points  $i_0$  and  $j_0$  are either isospectral or equivalent if and only if

$$\sum_q^{q_1} \langle i_0 | l_q \rangle^2 = \sum_q^{q_1} \langle j_0 | l_q \rangle^2, \quad l = 1, 2, \dots, L.$$

If we consider attachment of  $G'$  to  $G$  at the point  $j_0$  by the same