# Organic and Biological Chemistry

## Hückel Molecular Orbital π Resonance Energies. The Benzenoid Hydrocarbons

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**Abstract:** The HMO resonance energy per π electron (REPE) has been calculated for 40 benzenoid hydrocarbons. Compounds with an REPE of greater than 0.050β are found to be extremely stable. Compounds with an REPE of less than 0.050β are found to be of increasing reactivity (*e.g.*, in their ability to undergo addition reactions) as the REPE decreases. An excellent correlation is found between the REPE and the p band of the 40 compounds.

We have recently shown that the well-known failure of Hückel calculations to predict aromatic or antiaromatic character in hydrocarbons is due not to a fault of the Hückel wave functions, but instead to an erroneous identification of various "delocalization energies" with aromaticity. If resonance energy per π electron (REPE) is defined as the difference between the Hückel π energy and the π energy of a "localized structure" obtained in an additive manner using the empirical π bond energies listed in Table I, divided by the number of π electrons, a quantity is obtained that correlates well with experimental stability.[1] We present here the application of this method to a wide variety of totally benzenoid hydrocarbons.

**Table I.** Empirical π Bond Energies of Carbon-Carbon Double and Single Bonds

| Type of bond | ij | $E_{ij}^{\pi}$ |
|---|---|---|
| $CH_2{=}CH$ | 23 | 2.0000 |
| $CH{=}CH$ | 22 | 2.0699 |
| $CH_2{=}C$ | 22′ | 2.0000 |
| $CH{=}C$ | 21 | 2.1083 |
| $C{=}C$ | 20 | 2.1716 |
| $CH{-}CH$ | 12 | 0.4660 |
| $CH{-}C$ | 11 | 0.4362 |
| $C{-}C$ | 10 | 0.4358 |

### Results and Discussion

It is known that the linear annelation of unsaturated six-membered rings (the polyacenes) yields a series of hydrocarbons that show decreasing stability as the number of rings is increased.[2] Benzene is an extraordinarily stable compound, whereas pentacene is very reactive. On the other hand, angular annelation of unsaturated six-membered rings leads to hydrocarbons which are much more stable than their linear analogs; *e.g.*, picene (**20**) is considerably less reactive than pentacene (**15**). The REPE for the first eleven members of the polyacene series and nine members of the phenanthrene, chrysene, picene series is plotted against the number of rings in Figure 1. The REPE of the linear polyacenes falls off quite sharply initially, whereas the

**Table II.** Hückel MO Data for Compounds 1–40

| Compd | REPE $\times 10^3$ ($\beta$) | $\bar{\nu} \times 10^{-2}$,[a] $cm^{-1}$ | $\epsilon_{homo}$ ($\beta$) | Dewar's REPE,[b] eV | Deloc energy per π electron ($\beta$) |
|---|---|---|---|---|---|
| 1 | 65 | 480 | 1.000 | 0.145 | 0.333 |
| 2 | 55 | 351 | 0.618 | 0.132 | 0.368 |
| 3 | 60 | 400 | 0.704 | 0.142 | 0.365 |
| 4 | 47 | 267 | 0.414 | 0.114 | 0.380 |
| 5 | 55 | 342 | 0.605 | 0.138 | 0.389 |
| 6 | 51 | 300 | 0.445 | 0.131 | 0.407 |
| 7 | 42 | 212 | 0.295 | 0.101 | 0.385 |
| 8 | 50 | 278 | 0.452 | 0.127 | 0.394 |
| 9 | 53 | 313 | 0.520 | 0.138 | 0.400 |
| 10 | 53 | 317 | 0.568 | 0.138 | 0.399 |
| 11 | 56 | 352 | 0.684 | 0.147 | 0.404 |
| 12 | 48 | 230 | 0.347 | 0.131 | 0.412 |
| 13 | 53 | 302 | 0.497 | 0.142 | 0.417 |
| 14 | 49 | 231 | 0.371 | 0.129 | 0.411 |
| 15 | 38 | 172 | 0.220 | 0.091 | 0.388 |
| 16 | 45 | 221 | 0.327 |  | 0.397 |
| 17 | 51 | 286 | 0.473 | 0.134 | 0.404 |
| 18 | 51 | 285 | 0.492 | 0.134 | 0.404 |
| 19 | 49 | 274 | 0.405 |  | 0.402 |
| 20 | 53 | 304 | 0.502 | 0.140 | 0.406 |
| 21 | 52 | 312 | 0.550 | 0.140 | 0.406 |
| 22 | 52 | 304 | 0.535 | 0.140 | 0.406 |
| 23 | 51 | 258 | 0.439 | 0.142 | 0.428 |
| 24 | 45 | 231 | 0.291 | 0.121 | 0.421 |
| 25 | 45 | 218 | 0.303 |  | 0.411 |
| 26 | 45 | 199 | 0.265 |  | 0.413 |
| 27 | 49 | 230 | 0.351 |  | 0.417 |
| 28 | 53 | 293 | 0.539 | 0.147 | 0.441 |
| 29 | 41 | 182 | 0.199 | 0.112 | 0.408 |
| 30 | 42 | 181 | 0.244 |  | 0.398 |
| 31 | 46 | 238 | 0.348 |  | 0.403 |
| 32 | 51 | 266 | 0.447 |  | 0.410 |
| 33 | 47 | 246 | 0.296 |  | 0.425 |
| 34 | 48 | 225 | 0.285 |  | 0.427 |
| 35 | 43 | 165 | 0.194 |  | 0.414 |
| 36 | 42 | 151 | 0.177 |  | 0.431 |
| 37 | 38 | 171 | 0.128 |  | 0.407 |
| 38 | 44 | 189 | 0.269 |  | 0.405 |
| 39 | 47 | 212 | 0.394 |  | 0.408 |
| 40 | 40 | 157 | 0.194 |  | 0.409 |

[a] From ref 2. [b] From M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969); C. R. de Llano, Ph.D. Thesis, University of Texas, 1968.

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[1] B. A. Hess, Jr., and L. J. Schaad, *J. Amer. Chem. Soc.*, **93**, 305 (1971).

[2] E. Clar, "Polycyclic Hydrocarbons," Academic Press, New York, N. Y., 1964.

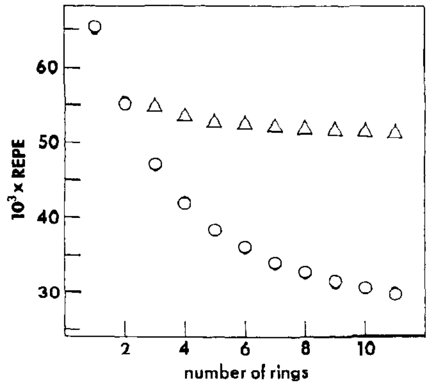

Figure 1. REPE ($\beta$) *vs.* the number of six-membered rings in polyacenes (○) and in the series phenanthrene, chrysene, picene, . . . (△).

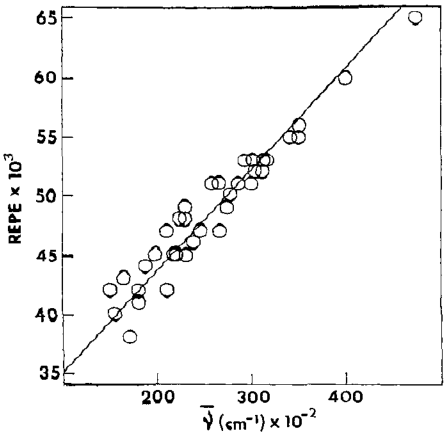

Figure 2. REPE ($\beta$) *vs.* p band frequency (cm$^{-1}$) for compounds **1–40**. The least squares line has standard deviation 20 $\times$ $10^2$ cm$^{-1}$.

REPE of the angular series decreases to a much lesser extent with increase in the number of rings which is in agreement with the above observations regarding their stability.

The REPE along with additional data (see below) is given in Table II for 40 benzenoid hydrocarbons. There is an excellent correlation between the reactivity of these hydrocarbons and their resonance energies. Compounds with an REPE greater than 0.050$\beta$, *e.g.*, benzene, naphthalene, phenanthrene, and triphenylene, generally do not undergo addition reactions with maleic anhydride and do not readily undergo photooxidation. Those compounds with an REPE less than 0.050$\beta$ appear to undergo addition reactions and photooxidation with increasing ease as the REPE decreases. 1,2-Benzanthracene (**8**) has an REPE of 0.050$\beta$ and undergoes addition with maleic anhydride only with great difficulty.[2] Zethrene with an REPE of 0.041$\beta$ reacts with maleic anhydride immediately at room temperature.[2]

One might wonder why pentacene is so reactive although it still appears to have substantial REPE (0.038$\beta$). Its reactivity is easily explained when one considers that it undergoes addition reactions at the 6 and 13 positions, *e.g.*, its addition reaction with maleic anhydride, to yield a 6,13-dihydropentacene derivative which now contains two naphthalene moieties. The formation of two new $\sigma$ bonds in addition to the increased REPE (0.055$\beta$) of the remaining $\pi$ electrons is more than enough to offset the loss of two $\pi$ bonds.

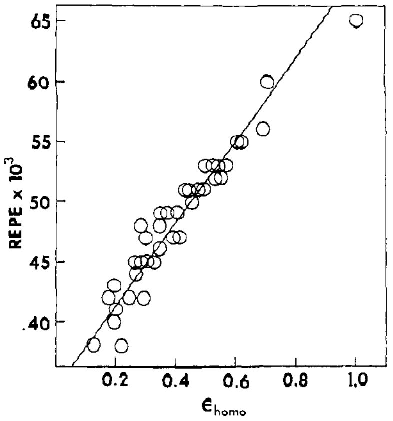

Figure 3. REPE ($\beta$) *vs.* energy of the HOMO ($\beta$) for compounds **1–40**. The least squares line is shown.

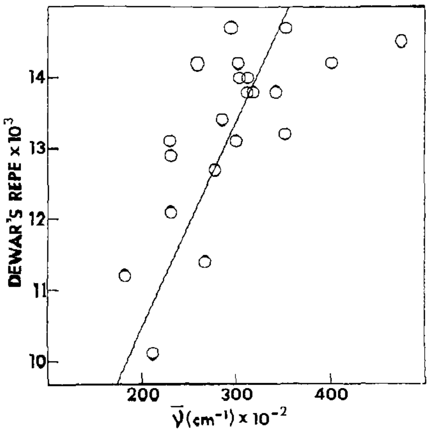

Figure 4. SCF MO resonance energy per $\pi$ electron (eV) *vs.* p band frequency (cm$^{-1}$). The least squares line has standard deviation 47 $\times$ $10^2$ cm$^{-1}$.

Clar has noted that the more highly colored a benzenoid hydrocarbon, the less stable it generally is.[2] He ascribes this relationship to a bathochromic shift of the p band as the stability decreases. We therefore plotted REPE *vs.* the p band of compounds **1–40** (Figure 2). A good linear relation is found. The p band is due to an electronic transition from the highest occupied molecular orbital (HOMO) to the lowest empty molecular orbital (LEMO). For alternant hydrocarbons the energy of the HOMO is the negative of that of the LEMO.[3] The frequency of the p band and therefore the REPE should then be proportional to the energy of the HOMO. Figure 3 shows that this expected relation does hold. We do not totally understand why there should be this connection between the REPE and HOMO (and therefore the REPE–p band relationship). Work is currently under way to determine the basis for the relationship.

We have also examined Dewar's semiempirical SCF MO resonance energies computed by the Pariser–Parr method to see whether they correlate with stability as well as do the Hückel REPE. A plot of Dewar's resonance energy per $\pi$ electron *vs.* p band frequency was made for a number of benzenoid hydrocarbons for which data were available.[4] It is apparent from Figure

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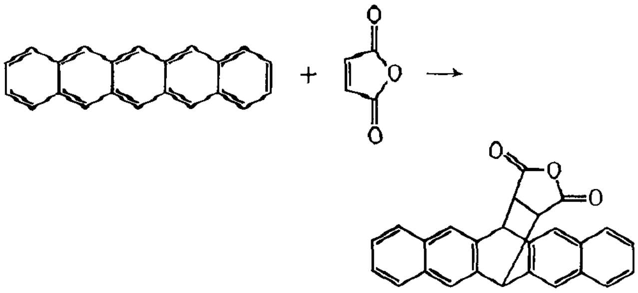
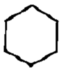
(3) C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940).

(4) (a) M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969); (b) see Table II, footnote *b*.



4 that the correlation is not as good as the HMO REPE–p band correlation. In light of the failure of the SCF MO resonance energies to give a good correlation with the p band of the benzenoid hydrocarbons and the very low SCF MO resonance energy for the nonalternate hydrocarbon azulene,[1,4] we feel that the easily obtained HMO resonance energies appear to be more satisfactory than do Dewar's SCF MO resonance energies.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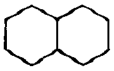
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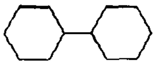
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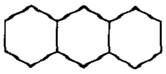
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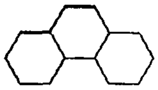
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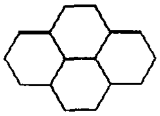
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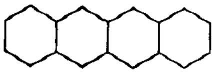
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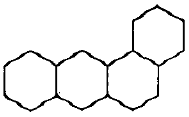
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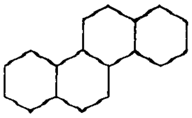
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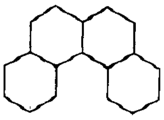
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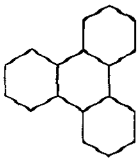
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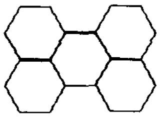
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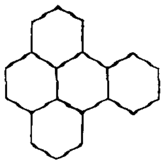
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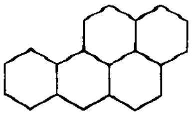
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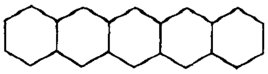
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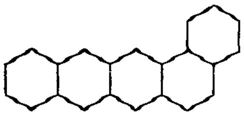
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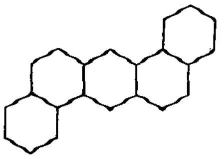
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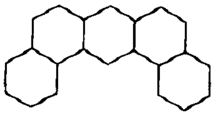
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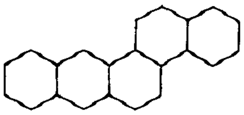
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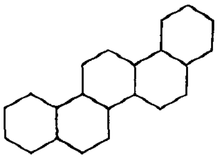
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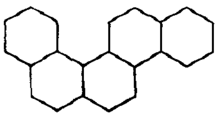
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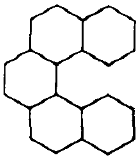
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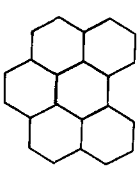
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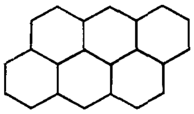
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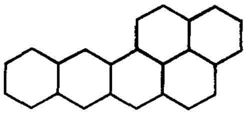
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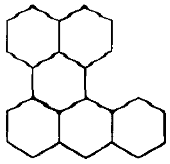
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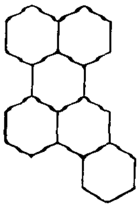
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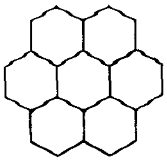
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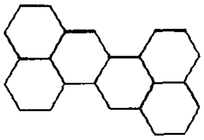
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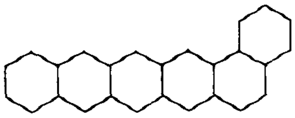
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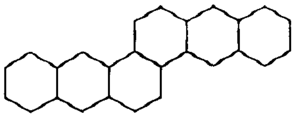
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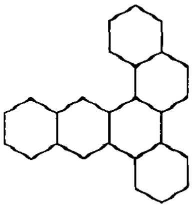
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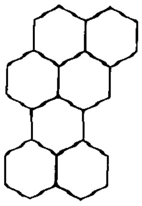
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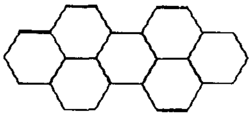
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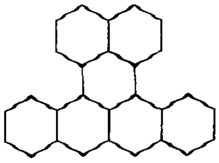
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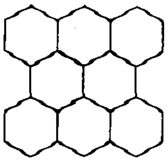
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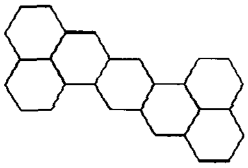
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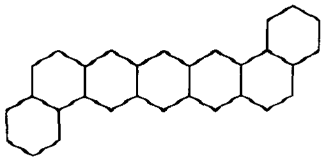
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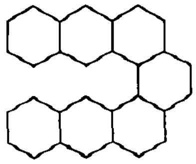
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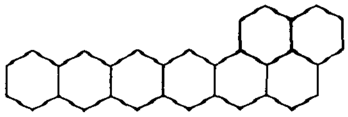
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Finally, the delocalization energy of compounds **1–40** was computed in the usual way as $E_\pi - 2n\beta$, where $n$ is the number of double bonds in the localized structure. Plotting delocalization energy per $\pi$ electron *vs.* p band frequency (Figure 5) shows again that delocalization energy is not useful in predicting the relative stability of benzenoid hydrocarbons.

In summary, we believe that HMO REPE of benzenoid hydrocarbons has a definite quantitative corre-

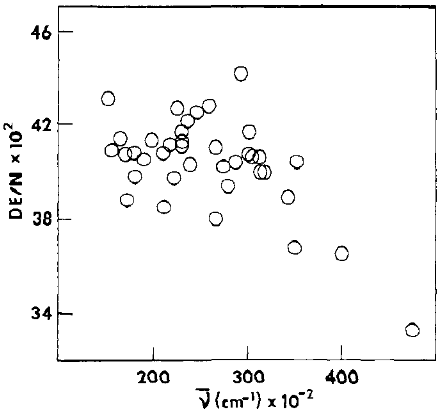

Figure 5. HMO delocalization energy per $\pi$ electron ($\beta$) *vs.* p band frequency (cm$^{-1}$) for compounds **1–40**.

lation with the stability of these compounds. The former treatment of HMO results (*i.e.*, delocalization energies) did not allow either qualitative or quantitative correlations of the types discussed above.

**Computational Details.** HMO resonance energies per $\pi$ electron were obtained as previously described.[1] In each case, the additive $\pi$ energy used in the resonance energy calculation was an average of individual additive $\pi$ energies of all possible resonance forms. For the larger molecules the determination of all resonance forms proved to be a difficult and tedious task. A computer program was written which, when given the ordinary HMO matrix, allowed the determination of not only all possible resonance forms, but also of the different kinds of bonds in each resonance form. In no case were the additive energies of resonance structures of the same compound significantly different. For example, coronene has 20 resonance structures which range from a low of 33.298$\beta$ to a high of 33.311$\beta$ in additive $\pi$ energy. These values correspond to REPE's respectively of 0.05307$\beta$ and 0.0525$\beta$.

**Description of Resonance Form Computer Program.** Embodied in the HMO matrix is the information needed to determine all resonance forms as well as the number of each type of bond in each resonance structure. Each nonzero off-diagonal element (*ij*) represents a carbon–carbon bond. For a given resonance structure some of these elements will represent double bonds and the remainder single bonds. A second matrix was constructed for each resonance structure by replacing each nonzero off-diagonal element in the original HMO matrix by either a 1 to indicate a single bond or a 2 for a double. To determine all resonance structures one has merely to determine all possible ways of constructing this matrix. This may be done in a systematic manner by assigning the first nonzero off-diagonal element in the first row to a double bond. The symmetrically placed element in the first column which corresponds to this bond is also noted as a double bond. One then proceeds to the next row and in a similar manner begins to the right of the diagonal in search of a bond (a nonzero element). If this row already contains a bond that has been assigned a double bond (*i.e.*, to the left of the diagonal), one proceeds to the next row (again beginning to the right of the diagonal), as each carbon atom may have only one double bond. Furthermore, if a nonzero element is found which is in a column that already has a double bond, it is left as a single bond and one proceeds in search of the next nonzero element.

If a bond is assigned as a double bond which cannot be a double bond, for example, the central bond of butadiene, a point will be reached in the matrix where a readily recognizable impossibility arises. For example, a row which contains no double bonds will be found (every carbon atom must have one and only one double bond in a conjugated system). If this happens, one proceeds in a reverse manner through the matrix until this error is found (see below). If one has not assigned any double bonds incorrectly, one can proceed as above to the last row and obtain a matrix representing one possible resonance structure. To obtain another possible resonance structure, one starts in the penultimate row of the above matrix (with the double bonds previously noted) at the right hand side and proceeds to the left along the row (only to the diagonal) in search of a previously noted double bond (if none is found in a row to the right of the diagonal, one goes to the row above). When a double bond is found it is changed to a single bond (along with the corresponding element in the lower left triangle) and another bond is searched for to the right of this bond on the same row. If one is found, then it is assigned a double bond (if possible) and one proceeds to finish the matrix as above and obtain another resonance structure. If no other bonds are found on that row, then one proceeds to the far right of the row above and searches to the left (only up to the diagonal) for a double bond. When one is found, the procedure is the same as above.

One continues this reverse process after each resonance structure is found until eventually all matrices corresponding to all resonance structures are found. All have been found when one reaches in the reverse process the top row and finds that there are no more elements in that row which can be assigned double bonds.

One uses these matrices to determine the number of each type of bond. The number of carbon atoms bonded to carbon atom *i* of the *ij* bond can be found by determining the number of nonzero elements in the *i*th row excluding the one representing the *ij* bond. Similarly, the number of carbon atoms attached to the carbon *j* of the *ij* bond is found by looking at column *j*. With the $\pi$ bond energies in Table I one may then obtain the additive bond energy.