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# Effect of Through Bond Interaction via Strained σ Bonds in Cyclohexane-1,4-dione Derivatives

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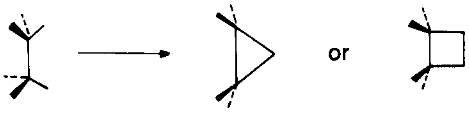
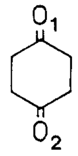
The He(I) photoelectron (PE) spectra of the cyclohexane-1,4-dione derivatives **3**–**8** have been recorded. The correlation of the first two bands shows an increase in the splitting from 0.2 eV in cyclohexane-1,4-dione to 0.6 eV in the case of **5** and **8** and 0.9 eV in the case of **2**. This increase in the splitting is interpreted in terms of an increase in the interaction between the n orbital and the σ frame. The extension of the investigations to systems with cyclobutene fragments (**12**–**15**) shows that these parts do not enhance the n/σ interaction. The assignment of the PE spectra is based on empirical correlations with the PE data of related molecules and on MINDO/3 calculations.

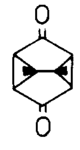
Recently we have demonstrated by means of He(I) photoelectron (PE) spectroscopy that the interaction between n- or π-orbitals and the σ skeleton can be increased by decreasing the basis orbital energy of the appropriate σ-system.[1,2] This can usually be done by replacing a normal C–C single bond with bonds incorporated into a strained system like a cyclopropane or a cyclobutane ring as shown below. A comparison of the PE spectra of



[2.2]paracyclophane and 1,2:9,10-dimethano[2.2]paracyclophane[1] as well as the comparison of the PE spectra of cyclohexane-1,4-dione (**1**) and 1,5-dimethyltetracyclo-[$3.3.0.0^{2,8}.0^{4,6}$]octane-3,7-dione (**2**) demonstrates the value of this concept.[2]



**1**



**2**

If we designate the 2p lone pairs at the oxygen centers 1 and 2 in **1** as $2p_1$ and $2p_2$ we can write down the following two linear combinations adopting a ZDO model:

$$n_+ = (1/(2^{1/2}))(2p_1 + 2p_2)$$

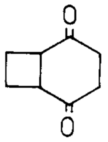
$$n_- = (1/(2^{1/2}))(2p_1 - 2p_2)$$

The increase of the interaction between the two lone pair combinations and the σ frame in changing from **1** to **2** has been demonstrated by PE investigations: For the 1,4-dione **1** the splitting between the first two bands (which corresponds to ionization events from $n_+$ and $n_-$) is found to be 0.2 eV[3] whilst for the 1,4-dione **2** an energy difference of 0.9 eV[2] is observed.

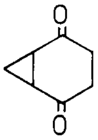
**Table I. Vertical Ionization Energies ($I_{v,j}$) of 3–8 Together with Calculated Orbital Energies ($-\epsilon_j$)**

| no. | band | $I_{v,j}$, eV | assignment | $-\epsilon_j$ (MINDO/3), eV |
|---|---|---|---|---|
| **3** | 1 | 9.4 | $12a''(n_-)$ | 9.35 |
| | 2 | 9.7 | $15a'(n_+)$ | 9.94 |
| **4** | 1 | 9.6 | $10a''(n_-)$ | 9.47 |
| | 2 | 9.8 | $14a'(n_+)$ | 10.15 |
| **5** | 1 | 9.0 | $7b_g(n_-)$ | 9.17 |
| | 2 | 9.7 | $9b_u(n_+)$ | 9.74 |
| **6** | 1 | 9.0 | $6a_2(n_-)$ | 9.17 |
| | 2 | 9.7 | $8b_1(n_+)$ | 9.73 |
| **7** | 1 | 9.3 | $12a''(n_-)$ | 9.29 |
| | 2 | 9.6 | $17a'(n_+)$ | 9.87 |
| **8** | 1 | 9.14 | $12a''(n_-)$ | 9.28 |
| | 2 | 9.70 | $17a'(n_+)$ | 9.91 |

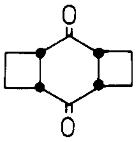
To investigate those examples where one or two σ-bonds of the cyclohexane ring are incorporated into a three- or four-membered ring we have recorded the PE spectra of known diones[4] **3**–**8**.



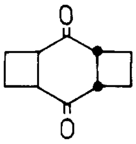
**3**



**4**



**5**



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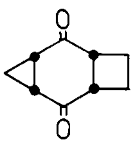
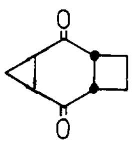


**7**



**8**

The series **9**–**13**[4–6] allows us to study the effect upon the splitting of the lone pairs by incorporating the C–C single and/or double bond into strained systems. The PE spectra of **14** and **15** are related to those of *p*-benzoquinone (**16**)[3,7,8]

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(5) (a) Garbish, E. W., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 4971. (b) Chapman, D. D.; Musliner, W. J.; Gates, J. W. *J. Chem. Soc. C* **1969**, 124.

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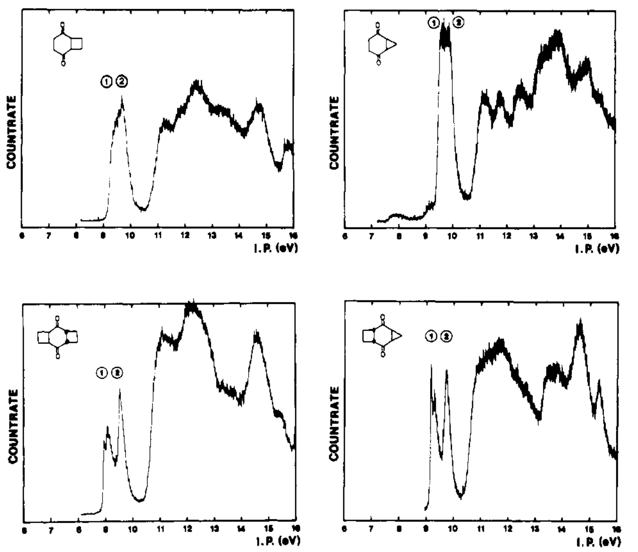
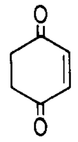
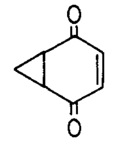


**Figure 1.** He(I) PE spectra of **3**, **4**, **6**, and **8**.

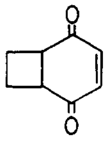
and tetramethyl-*p*-benzoquinone (**17**)[8] which have been discussed in the literature.



**9**



**10**



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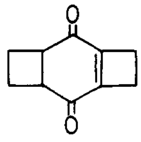
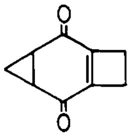
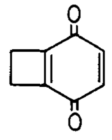


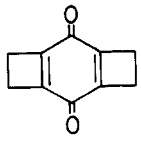
**12**



**13**



**14**



**15**

**PE Spectra of 3–8.** In Figure 1 the PE spectra of the representative diones **3**, **4**, **6**, and **8** are shown. The first ionization energies of diones **3–8** are shown in Table I.

The PE spectra of **3** and **4** show two very close lying peaks below 10 eV whilst in **5**, **6**, and **8** the bands are clearly separated and even exhibit some fine structure. To interprete the spectra we compare the first bands with the results of molecular orbital calculations thus assuming Koopmans' approximation ($I_{v,j} = -\epsilon_j$).[9] This approximation states that the experimentally determined vertical ionization energy ($I_{v,j}$) is equal to the calculated orbital energy derived for the ground state. To calculate the orbital energies we use the MINDO/3 model[10] which has been proven to be reliable for other ketones. Since the geometry of **3–8** is not known we have calculated it by minimizing the heat of formation ($\Delta H_f$) with respect to the geometrical parameters assuming at least $C_s$ symmetry. The results are provided as supplementary material.

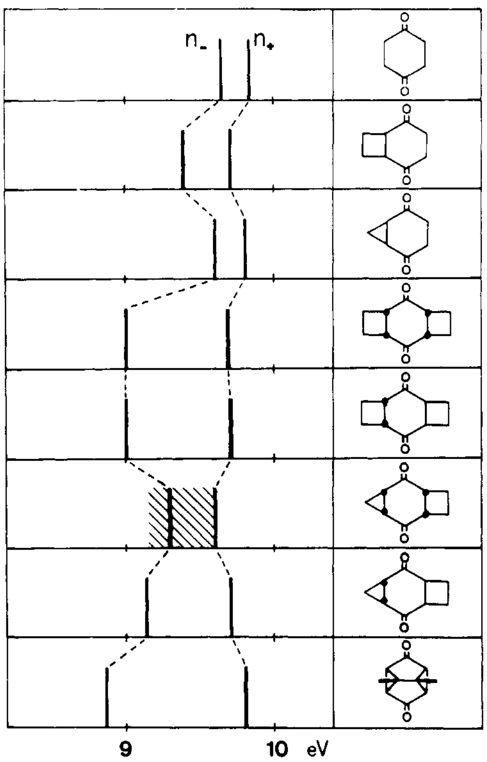


**Figure 2.** Correlation of the first two PE bands of **1–8**.

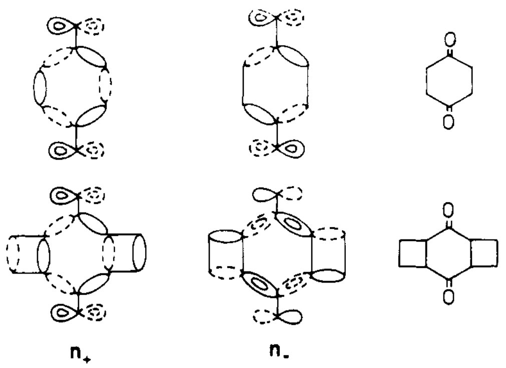


**Figure 3.** Schematic representations of the two highest occupied MO's ($n_-$,$n_+$) of **1** and **5**. Double contour lines indicate higher density.

The calculated orbital energies together with the irreducible representations of the corresponding wave functions are given in Table I. In Figure 2 we have correlated the first two bands of **3–8** with those of **1** and **2** adopting the assignment given in Table I. In all cases the $n_-$ combination is predicted to be above the $n_+$ combination. The calculations reproduce the experimentally observed trends found as they predict two narrowly separated MO's for **3** and **4** and a more widely separated $n_-$ and $n_+$ for **5–8** (see Table I). This increase in the energy difference between $n_-$ and $n_+$ can be attributed to the enhanced interaction between the $n_-$ linear combination and the $\sigma$ frame while the $n_+/\sigma$ interaction remains essentially constant in comparing **1** with **5–8** and **2**. This is demonstrated in Figure 3. When comparing the first bands in the syn/anti isomers **5**, **6**, and **7**, **8**, respectively, we notice no difference between the tricyclo[6.2.0.0$^{3,6}$]decane-2,7-diones **5** and **6** whereas relatively large differences are observed for the first bands of the tricyclo[5.2.0.0$^{3,5}$]nonane-2,6-diones **7** and **8**. The difference between **7** and **8** is partly because the first band of **7** shows a Gaussian shape while for **8** the values for the vertical and adiabatic ionization energies are almost identical. This observation can be rationalized by

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[8] Dougherty, D.; Mc Glynn, S. P. *J. Am. Chem. Soc.* **1977**, *99*, 3234.

[9] Koopmans, T. *Physica* **1934**, *1*, 104.

[10] Bingham, R.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285. We used a program published by P. Bischof.[11]

[11] Bischof, P. *J. Am. Chem. Soc.* **1976**, *98*, 6844.

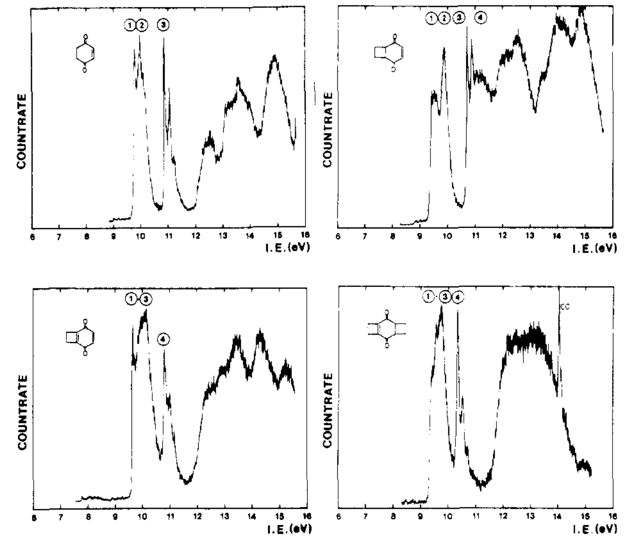

**Figure 4.** He(I) PE spectra of 9, 11, 14, and 15.

Table II. Vertical Ionization Energies ($I_{v,j}$) of 9–13 Together with Calculated Orbital Energies ($-\epsilon_j$) Determined by MINDO/3

| no. | band | $I_{v,j}$, eV | assignment | $-\epsilon_j$ (MINDO/3), eV |
|---|---|---|---|---|
| **9** | 1 | 9.77 | 9a″(n₋) | 9.59 |
| | 2 | 9.98 | 12a′(n₊) | 10.35 |
| | 3 | 10.82<br>11.06 | 11a′(π) | 10.89 |
| **10** | 1 | 9.64 | 9a″(n₋) | 9.51 |
| | 2 | 10.0 | 14a′(n₊) | 10.19 |
| | 3 | 10.77<br>10.96 | 12a′(π) | 10.84 |
| | 4 | 11.2 | 13a′(ω) | 10.66 |
| | 5 | 11.9 | 8a″(ω) | 11.17 |
| **11** | 1 | 9.5 | 11a″(n₋) | 9.38 |
| | 2 | 9.9 | 15a′(n₊) | 9.97 |
| | 3 | 10.69<br>10.87 | 13a′(π) | 10.83 |
| | 4 | 11.2 | 10a′(ω) | 11.0 |
| **12** | 1 | $9.2_5$ | 13a″(n₋) | 9.09 |
| | 2 | $9.5_5$ | 18a′(n₊) | 9.60 |
| | 3 | 9.9 | 17a′(π) | 9.96 |
| | 4 | 10.0 | 16a′(ω) | 10.43 |
| **13** | 1 | 9.38 | 11a″(n₋) | 9.19 |
| | 2 | 9.65 | 17a′(n₊) | 9.70 |
| | 3 | 10.0 | 16a′(π) | 9.96 |
| | 4 | 11.0 | 15a′(ω) | 10.42 |

only small changes in geometry in the first ionic state for 8 but with larger changes for 7.

**PE Spectra of 9–15.** In Figure 4 the PE spectra of the representative diones 9, 11, 14, and 15 are shown. The first ionization energies of diones 9–15 are collected in Table II.

In the PE spectra of 9–11 we can observe three bands below 11 eV. A comparison with the PE spectrum of 1 (see Figure 5) immediately allows us to assign the first three bands of 9 to ionization events from $n_-$, $n_+$, and $\pi$ orbitals.

The effect of lone pair splitting as a function of strain exerted on the C–C single bond of the cyclohexene-1,4-dione system by incorporating it into a three- or four-membered ring can be studied by comparing the first bands of the PE spectra of 9 with those of 10 and 11. From this comparison we infer an increase in the energy difference of the first two bands of both compounds by about 0.15 eV. We find no difference between three- and four-membered rings.

If the double bond of the cyclohexene-1,4-dione moiety is made part of a strained system, as in 12 and 13, we observe that bands 1–3 are closer together and that all three are shifted to lower ionization energies when compared with 10 and 11. This shift is anticipated due to the hyperconjugative and inductive effect of the additional $C_2H_4$ bridge.

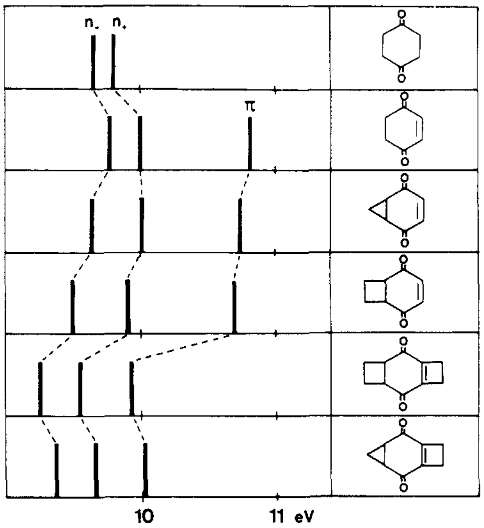

**Figure 5.** Correlation of the first PE bands of 1 and 9–13.

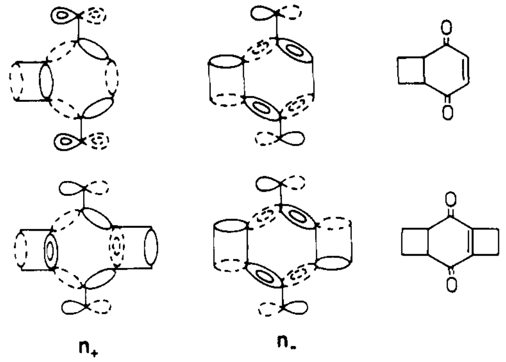

**Figure 6.** Schematic representation of the two highest occupied MO's ($n_-$, $n_+$) of 11 and 12. Double contour lines indicate higher density.

To assign the band sequence empirically we compare the first ionization energy of ethylene (10.51 eV[7a]) with that of cyclobutene (9.6 eV[12]). From this we infer a shift of 0.9 eV for the $\pi$ band which leads us to correlate band 3 of the PE spectrum of 12 (9.3 eV) with band 3 of the PE spectrum of 11 (10.7 eV) and this leaves the n orbitals in the PE spectrum of 12 and 13 as bands 1 and 2 (see Figure 5). The shift toward lower energy (0.3 eV) between bands 1 and 2 of 11 and 12 is due to a shift of the center of gravity of bands 1 and 2 of 5 compared to bands 1 and 2 of 3 (see Figure 2).

In contrast to the comparison of 3 with 5 and 6 where the introduction of the second four-membered ring has lead to an increase in the splitting of the first two bands we encountered a slight decrease. This observation can be rationalized if we compare the wave functions for $n_-$ and $n_+$ of 11 and 12. Both are shown schematically in Figure 6. In contrast to the situation to 3–5 (Figure 3) where we notice an increase of $\sigma$ participation for $n_-$ only, the com-

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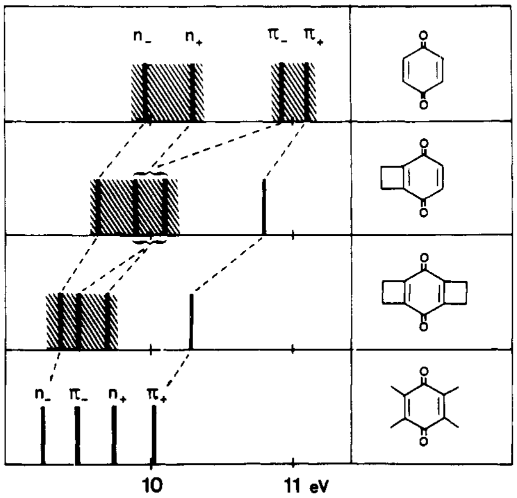

**Figure 7.** Correlation of the first four PE bands in the spectra of *p*-benzoquinone with those of **14**, **15**, and **17**.

parison of **11–12** shows an increase in $\sigma$/n interaction for both linear combinations.

A comparison between measured ionization energies and calculated orbital energies of **9–13** (Table II) shows a remarkably good agreement. The only discrepancy we notice is for dione **10** where the MINDO/3 calculation places the Walsh type orbital localized on the three-membered ring (13a′) at lower orbital energies than the $\pi$ orbital (12a′). Such a discrepancy is encountered for strained systems containing three-membered rings. The calculated heat of formation and the geometrical parameters of **9–15** are provided as supplementary material.

The PE spectra of the *p*-benzoquinone derivatives **14** and **15** in Figure 4 show three strongly overlapping bands in the low energy part clearly separated from a fourth band below 11 eV with vibrational fine structure (0.20 eV). To assign these spectra empirically it seems logical to correlate the first bands with those of *p*-benzoquinone (**16**). The assignment of the PE spectrum of **16** is, however, still a matter of controversy[7,8] and therefore our assignment of bands 2 and 3 of **14** and **15** must remain tentative. Based on our studies of **11** and **12** (see above) and comparing the PE spectra of **16** and **14** it is reasonable to assume a strong shift (~0.8–0.9 eV) for one $\pi$ band and a small shift (~ 0.3–0.4 eV) for $n_-$, $n_+$, and the other $\pi$ band. Adopting the orbital sequence $n_-$, $n_+$, $\pi_-$, and $\pi_+$ for **16** we arrive at the correlation given in Figure 7. This leads to the assignment of $n_-$ to band 1 and $\pi_+$ to band 4 of **14**. Because of the close proximity and the missing of any difference in shape or fine structure the assignment of bands 2 and 3 is difficult. If we adopt the assignment $\pi_-$ on top of $n_+$ for **15** we obtain the same orbital sequence as suggested for **17**,[8] i.e., $n_-$, $\pi_-$, $n_+$, and $\pi_+$ (see Figure 7). The alternative sequence, $n_-$, $n_+$, $\pi_-$, and $\pi_+$, however, cannot be ruled out for **15** as well as for **17**.

**Table III. Vertical Ionization Energies ($I_{v,j}$) of 14 and 15 Together with Calculated Orbital Energies ($-\epsilon_j$) Determined by MINDO/3**

| no. | band | $I_{v,j}$, eV | assignment | $-\epsilon_j$ (MINDO/3), eV |
|---|---|---|---|---|
| **14** | 1 | 9.64 | $8b_2(n_-)$ | 9.30 ($8b_2$) |
| ($C_{2v}$) | 2 | 9.9 | $11a_1(n_+)$ | 9.81 ($11a_1$) |
| | 3 | 10.1 | $4b_1(\pi)$ | 10.05 ($4b_1$) |
| | 4 | 10.78 | $3b_1(\pi)$ | 10.86 ($3b_1$) |
| **15** | 1 | 9.4 | $4b_{3g}(n_-)$ | 9.01 ($4b_{3g}$) |
| ($D_{2h}$) | 2 | 9.5 | $2b_{1g}(\pi_-)$ | 9.54 ($6b_{2u}$) |
| | 3 | 9.7 | $6b_{2u}(n_+)$ | 9.84 ($2b_{1g}$) |
| | 4 | 10.3 | $3b_{3u}(\pi_+)$ | 10.15 ($3b_{3u}$) |
| | | 10.5 | | |

The calculated orbital energies agree remarkably well with the experimentally determined ionization energies. Due to the small energy differences for $6b_{2u}$ and $2b_{1g}$ of **15** a definite assignment of bands 2 and 3 of **15** is not possible.

**Concluding Remarks.** The assignment given in Tables I–III gives a consistent interpretation of the PE spectra of a large series of cyclohexane-1,4-diones and cyclohexene-1,4-diones. Since the empirical assignment and that based on the comparison with calculations are compatible, the orbital sequence suggested for **3–13** seems very likely. The experiments demonstrate that the replacement of an unstrained C–C single bond by one of a strained system such as cyclopropane or cyclobutane enlarges the interaction between the 2p lone pairs and the $\sigma$ frame work. Interesting conformational dependent effects in the case of cyclopropane fragments have been uncovered.

## Experimental Section

Known compounds **3–15** were described in the literature.[4-6] The He(I) PE spectra of the analytically pure compounds were measured on a Perkin Elmer PS 18 and on a Leybold-Heraeus UPG 200 spectrometer. For the calibration we used Ar and Xe. A resolution of about 20 meV of the $^2P_{3/2}$ Ar line was obtained. All samples had to be heated between 40–70 °C. For **15** loss of CO was observed during the measurement.

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**Registry No.** **3**, 54338-82-8; **4**, 60582-65-2; **5**, 87305-43-9; **6**, 87305-42-8; **7**, 94499-48-6; **8**, 94595-48-9; **9**, 4505-38-8; **10**, 53735-22-1; **11**, 77627-56-6; **12**, 94499-49-7; **13**, 94499-50-0; **14**, 77627-49-7; **15**, 87258-06-8.

**Supplementary Material Available:** A listing of the calculated heat of formation and geometrical parameters of **3–15** (3 pages). Ordering information is given on any current masthead page.