Fulvenones and Isoelectronic Diazocyclopolyenes: Theoretical Studies of Structures and Stabilization

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Abstract: Isodesmic energy comparisons of 6-31G* // 6-31G* calculations for the fulvenes 1-3 and fulvenones 4-6 show significant destabilization for triafulvenone (4, -17.1 kcal) and heptafulvenone (6, -5.1 kcal/mol) and stabilization for pentafulvenone (5, 4.1 kcal/mol). These effects are attributed to enhanced antiaromatic destabilization in 4 and 6 compared to the corresponding fulvenes and enhanced aromatic stabilization in pentafulvenone (5) compared to pentacyclafulvene (3). Analysis of dipole moments, atomic charges, and bond lengths provides further evidence for these aromaticity effects. Similar evidence is found for antiaromatic destabilization upon fluorine substitution in the exocyclic methylene group of triafulvene. Diazocyclopentadiene (7), diazocycloheptatriene (8), and diazocycloheptatrienone (9) are isoelectronic with the corresponding fulvenones 4-6, respectively, and show the corresponding destabilization and stabilization effects.

The fulvenes, especially triafulvene (1), pentafulvene (2), and heptafulvene (3), have attracted intense interest because of their unique conjugated structures.\(^{1-6}\) The question of the aromatic/antiaromatic character of these and similar rings has attracted particular attention.\(^1\)

The corresponding ketenes 4-6 may be referred to as fulvenones, with specific names of triafulvenone (4), pentafulvenone (5), and heptafulvenone (6).\(^2\) Of these, 5\(^{1-3}\) and 6\(^8\) have been studied.


(2) Alternative names are cyclopropylideneketene (4), cyclopentadienylideneketene (5), and cycloheptatrieneketene (6).
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experimentially, as well as the benzo derivatives of 5,4\textsuperscript{5}. By contrast, there have apparently been no experimental studies of 4, \textsuperscript{4} although there are theoretical studies of its structure\textsuperscript{7b} and reaction with protons and H\textsubscript{2}O.\textsuperscript{7c}

Derivatives of compound 5 have major practical applications in photoreactors\textsuperscript{8} and have been the object of many experimental studies,\textsuperscript{8,9} while 6 has been generated and utilized as a synthetic intermediate\textsuperscript{8} but has not been studied theoretically. Despite the possible influence of aromaticity/antiaromaticity effects on the structure and stability of 4–6, there has been no systematic study of this problem, which is the topic of this investigation. The diazo compounds 7–9, iso-electrostatic to 4–6, respectively, are of similar interest and have also been examined.

Ketenes have recently been of interest to us\textsuperscript{8} and are also being actively examined by others both experimentally\textsuperscript{9} and theoretically.\textsuperscript{7,10} We have found that ab initio calculations of the stabilities and energies of ketenes\textsuperscript{10} and diazo compounds\textsuperscript{8} are quite informative as to the influence of structural variables on the geometries, stabilities, and reactivities of these compounds. Therefore, we have extended these investigations to the fulvenes 1–3, the fulvenones 4–6, the diazo compounds 7–9, and for comparative purposes some fluorofulvenes and some open-chain analogues. Two recent theoretical studies of 4 have appeared,\textsuperscript{11a,11b} but these do not address the question of aromaticity; otherwise, no experimental or theoretical examinations of the geometries and energies of these fulvenones and substituted fulvenones are available.

Methodology and Results
Calculations were carried out using the GAUSSIAN 98\textsuperscript{11c} package modified by the MONSTERGAUSS program\textsuperscript{11d} using Apollo DN1000 and IBM 6000 minicomputers. Gradient techniques using the Optimally Conditioned method\textsuperscript{11e} were used for geometry optimization, and all stationary points were optimized at the Hartree–Fock (HF) level using the split-valence 6-31G* basis set,\textsuperscript{11f} with the constraint of planar ring structures. The orders (number of negative diagonal elements of the Hessian matrix) of all critical points were determined at the 3-21G and 6-31G* levels by analytical differentiation of the restricted Hartree–Fock wave function and were found to equal zero in all cases except diazocyclopropane, difluorotrifulvenone, divinylethylene, divinylene, 6,9, and 10, which have one such element. The structures with order zero are thus true energy minima for the planar structures, while for those with order one the true minima are presumably nonplanar.

The structures and energies of all the substrates were calculated at the 3-21G//3-21G and 6-31G*//6-31G* levels as summarized in Tables I and II. Various isodesmic reactions were used to assess the stabilities of the fulvenes and fulvenones, as presented in Table II. More detailed energies, geometries, and dipole moments are given in Tables III and IV (supplementary material). There have been other calculations of the structures of 1\textsuperscript{11g} and 2,3.\textsuperscript{11h}

Atomic charges were calculated from the Mulliken population analysis\textsuperscript{11i} and are given in Table V (supplementary material). Charges calculated by the Mulliken population analysis have been criticized, and alternative methods for the calculation of charges have been proposed, including that of Bader for partitioning molecules into atoms,\textsuperscript{11j} the natural population analysis,\textsuperscript{11k} and generalized atomic polar tensors (GAPT).\textsuperscript{11l} However, Bader’s method itself has been criticized,\textsuperscript{11m} and the GAPT method is admitted\textsuperscript{11n} to give unrealistic results when applied to compounds such as ketenes with multiple bonds. While a systematic comparison and evaluation of charges calculated by these different methods is desirable, we believe that trends obtained from the Mulliken analysis are informative, although the quantitative values should be regarded with caution.

The isodesmic energy changes as shown in Table II in general do not vary greater than the values calculated with the 3-21G and 6-31G* basis sets. The same behavior has been found for ketenes\textsuperscript{11n} and diazomethanes\textsuperscript{11b} and suggests that these energies will not change significantly with even higher level calculations. Further single-point energy calculations were carried out at the HF/6-31G**/MP2/6-31G**/MP3/6-31G** and MP4/6-31G** levels using 6-31G* geometries to give \( \Delta E \) values (kcal/mol) of -17.3, -14.2, -13.9, and -13.0, respectively, for entry 1 and -23.0, -25.5, -22.9, and -21.7, respectively, for entry 17 (Tables VII and VIII of the supplementary material). These results suggest that major changes in the results are not expected at higher levels of theory.
Table I. 6-31G* Optimized C-C, C-O, C-F, and C-N Bond Distances (Å) and Bond Angles (deg) for Fulvenones, Fulvenes, and Diazo Compounds

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Distances (Å)</th>
<th>Bond Angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>1.279</td>
<td>1.275</td>
</tr>
<tr>
<td>C-O</td>
<td>1.153</td>
<td>1.166</td>
</tr>
<tr>
<td>C-F</td>
<td>1.504</td>
<td>1.157</td>
</tr>
<tr>
<td>C-N</td>
<td>1.157</td>
<td>1.166</td>
</tr>
</tbody>
</table>

*McAllister and Tidwell*
Table II. Energies (hartrees) (6-31G*//6-31G*) for Fulvenones and Fulvenes and Stabilization Energies (ΔE, kcal/mol) for Some Isodesmic Reactions of Fulvenones

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fulvenones</th>
<th>Fulvenes</th>
<th>Stabilization Energies (ΔE, kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-227.3303 + CH₃CH₂CH₂</td>
<td>-153.6658 + CH₃CH₂CO</td>
<td>3-21G: -13.2 6-31G*: -17.1</td>
</tr>
<tr>
<td>2</td>
<td>-229.5768 + CH₃CH₂</td>
<td>-154.8873 + CH₃CH₂CO</td>
<td>2.4 0.5</td>
</tr>
<tr>
<td>3</td>
<td>-215.9215 (Z) 215.9205 (E) + CH₃CH₂CHF</td>
<td>-252.5106 + CH₃CH₂CH₂</td>
<td>5.4 5.7</td>
</tr>
<tr>
<td>4</td>
<td>-215.9264 + CH₃CH₂CHF</td>
<td>-253.7350 + CH₃CH₂CH₂</td>
<td>1.7 1.4</td>
</tr>
<tr>
<td>5</td>
<td>-314.7780 + CH₃CF₂</td>
<td>-351.3599 + CH₃CH₂CH₂</td>
<td>8.6 10.3</td>
</tr>
<tr>
<td>6</td>
<td>-266.4275 + CH₃CH₂</td>
<td>-352.5909 + CH₃CH₂CH₂</td>
<td>1.5 1.9</td>
</tr>
<tr>
<td>7</td>
<td>-267.6264 + CH₃CH₂</td>
<td>-192.7461 + CH₃CH₂CO</td>
<td>3.4 5.2</td>
</tr>
<tr>
<td>8</td>
<td>-304.3387 + CH₃CH₂</td>
<td>-193.9424 + CH₃CH₂CO</td>
<td>1.2 2.3</td>
</tr>
<tr>
<td>9</td>
<td>-305.5091 + CH₃CH₂</td>
<td>-230.6444 + CH₃CH₂CO</td>
<td>5.1 4.1</td>
</tr>
<tr>
<td>10</td>
<td>-305.5091 + CH₃CH₂</td>
<td>-231.8240 + CH₃CH₂CO</td>
<td>-1.1 -1.6</td>
</tr>
<tr>
<td>11</td>
<td>-305.4814 + CH₃CH₂CHF</td>
<td>-329.4939 + CH₃CH₂CH₂</td>
<td>0.3 0.3</td>
</tr>
<tr>
<td>12</td>
<td>-343.7353 + CH₃CH₂CF₂</td>
<td>-425.3513 + CH₃CH₂CH₂</td>
<td>-0.8 -0.2</td>
</tr>
<tr>
<td>13</td>
<td>-361.2164 + CH₃CH₂</td>
<td>-231.7937 + CH₃CH₂CO</td>
<td>-0.2 0.0</td>
</tr>
<tr>
<td>14</td>
<td>-343.7353 + CH₃CH₂</td>
<td>-269.6818 + CH₃CH₂CO</td>
<td>-3.2 -3.8</td>
</tr>
<tr>
<td>15</td>
<td>-361.2164 + CH₃CH₂</td>
<td>-307.5368 + CH₃CH₂CO</td>
<td>-5.2 -5.1</td>
</tr>
<tr>
<td>16</td>
<td>-424.9962 + CH₃CH₂</td>
<td>-351.3457 + CH₃CH₂CO</td>
<td>-19.7 -23.4</td>
</tr>
<tr>
<td>17</td>
<td>-223.4425 + CH₃CH₂</td>
<td>-186.8805 + CH₃CH₂N₂</td>
<td>-15.1 -22.8</td>
</tr>
<tr>
<td>18</td>
<td>-224.6861 + CH₃CH₂</td>
<td>-231.8240 + CH₃CH₂N₂</td>
<td>-2.5 -6.4</td>
</tr>
<tr>
<td>19</td>
<td>-301.6325 + CH₃CH₂</td>
<td>-231.8240 + CH₃CH₂N₂</td>
<td>1.2 -0.3</td>
</tr>
<tr>
<td>20</td>
<td>-300.4659 + CH₃CH₂</td>
<td>-186.8805 + CH₃CH₂N₂</td>
<td>11.6 7.8</td>
</tr>
<tr>
<td>21</td>
<td>-327.3450 + CH₃CH₂</td>
<td>-231.8240 + CH₃CH₂N₂</td>
<td>1.4 -0.5</td>
</tr>
</tbody>
</table>
A comparison of experimental bond distances\textsuperscript{12} for the fulvenes 1–3 with the calculated (6-31G*) values given in Table VI (supplementary material). The calculated bond distances differ from the experimental values, by amounts that vary from 0.007 to 0.024 Å. Comparable behavior was found for acyclic ketenes.\textsuperscript{44} It was found\textsuperscript{13} that the MP2/6-31G* basis set including electron correlation gave a calculated geometry for I that agreed with the experimental structure within the experimental error of the measurement. Unfortunately calculations at this level for the larger molecules 4–6 are not feasible for us at this time. The calculated dipole moments are in rather good agreement with experiment, although in some cases the calculated values are somewhat larger. The same trend was found with acyclic ketenes.\textsuperscript{56} Despite two reports of microwave studies of cyclopropyldenemethanone (10),\textsuperscript{12,56} no experimental geometries of cycloalkylidene ketenes or fulvenones have been reported.

### Energies

Recently\textsuperscript{56} we have been able to account for the effect of substituents on the stability of ketenes by using the isodesmic reaction of eq 1 and the ketene energies calculated by ab initio methods using the 6-31G*/6-31G* basis set. It was found that \( \Delta E \) for this reaction could be correlated by substituent-group electronegativity parameters \( X_{\text{RE}} \) as reported by Boyd and Edgoome.\textsuperscript{11} Further analysis of the results suggested that ketenes are destabilized by \( \pi \)-acceptor substituents and stabilized by \( \pi \)-donors and \( \sigma \)-donors.\textsuperscript{66}

To examine the factors that contribute to the stability of the fulvenones, we have also used the 6-31G*/6-31G*-calculated energies and isodesmic reactions according to reaction 2, as summarized in Table II.

\[
\text{R}_2\text{C} = \text{C} = \text{O} + \text{CH}_2\text{CH} = \text{CH}_2 \rightarrow \text{CH}_2\text{CH} = \text{C} = \text{O} + \text{R}_2\text{C} = \text{C} = \text{H}_2 \quad (2)
\]

Ketenes are negatively charged on \( \text{C}_2 \),\textsuperscript{66} and this leads to the prediction that trifulvenone may be destabilized by antiaromatic effects. The calculated \( \Delta E \) for the isodesmic reaction of trifulvenone (eq 3) shows this ketene is indeed destabilized by 17.1 kcal/mol. This effect is not due to some ring-strain effect of the cyclopropyl ring, as the saturated analogue 10 shows a net stabilization of 0.5 kcal/mol (eq 4).

\[
\begin{align*}
\text{R}_2\text{C} = \text{C} = \text{O} + \text{CH}_2\text{CH} = \text{CH}_2 & \rightarrow \text{CH}_2\text{CH} = \text{C} = \text{O} + \text{R}_2\text{C} = \text{C} = \text{H}_2 \quad (3) \\
\text{R}_2\text{C} = \text{C} = \text{O} + \text{CH}_2\text{CH} = \text{CH}_2 & \rightarrow \text{CH}_2\text{CH} = \text{C} = \text{O} + \text{R}_2\text{C} = \text{C} = \text{H}_2 \quad (4)
\end{align*}
\]

The small net energy change shown in eq 4 may result from a combination of opposing stabilizing and destabilizing effects on the ketene 10. Thus, the cyclopropyl ring is \( \sigma \)-electron-withdrawing by hybridization effects,\textsuperscript{14} and electronegative groups are destabilizing as ketene substituents.\textsuperscript{66} However, to the extent that 10 has the character of a cyclopropyl anion, a stabilized species,\textsuperscript{14a,b} it would also be stabilized, and 10 also has the orbital arrangement of the cyclopropylidene cation 12, which is suggested to be stabilized by delocalization from the C–C \( \sigma \)-bonds of the cyclopropyl to the vacant \( \pi \)-orbital of the vinyl cation.\textsuperscript{14c}

\[
\text{R}_2\text{C} = \text{C} = \text{O} + \text{CH}_2\text{CH} = \text{CH}_2 \rightarrow \end{align*}
\]

Some support for stabilizing influences in 10 is seen in the isodesmic comparison of eq 5, which shows that 10 is favored by 2.8 kcal/mol in comparison to the 4-membered ring analogue 14. This argument assumes that stabilization of 13 relative to 11 does not cause the observed effect.

\[
\begin{align*}
\text{R}_2\text{C} = \text{C} = \text{O} + \text{CH}_2\text{CH} = \text{CH}_2 & \rightarrow \text{CH}_2\text{CH} = \text{C} = \text{O} \quad (5) \\
\end{align*}
\]

To probe the origin of the destabilizing effect of the carbonyl group of 4 compared to other electron acceptor substituents, the effects of fluorine have also been examined.\textsuperscript{15a} There are only small effects on methylenecyclopropane (11), with destabilizations of 1.4 and 1.9 kcal/mol for one and two fluorines, respectively (entries 4 and 6, Table II). Thus, effects due to electron acceptor substituents on the methylenecyclopropane structure appear to be small. However, fluorine are strongly destabilizing to triafulvene (1) and by almost additive amounts for one and two fluorines (5.7 and 10.3 kcal/mol, respectively). The fluorines resemble the carbonyl group in being electronegative and in their \( \sigma \)-donor ability. The latter effect leading to resonance structure 15 would result in 4\( \pi \)-electron antiaromatic destabilization, and evidently this causes the large net destabilization.

\[
\begin{align*}
\text{R}_2\text{C} = \text{C} = \text{O} + \text{CH}_2\text{CH} = \text{CH}_2 & \rightarrow \text{CH}_2\text{CH} = \text{C} = \text{O} \quad (6) \\
\end{align*}
\]

Even heptafulvenone (6) shows destabilization of 5.1 kcal/mol by the isodesmic comparison of eq 7. This is consistent with antiaromatic destabilization of 6, although the effect is considerably attenuated relative to 4.

\[
\begin{align*}
\text{R}_2\text{C} = \text{C} = \text{O} + \text{CH}_2\text{CH} = \text{CH}_2 & \rightarrow \text{CH}_2\text{CH} = \text{C} = \text{O} \quad (7) \\
\end{align*}
\]

\textsuperscript{(13) Boyd, R. J.; Edgoome, K. E. J. Am. Chem. Soc. 1988, 110, 4182–4186.}
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Scheme I. Dipole Moments (Debye, in Parentheses) of Triafulvenes and Analogues

\[
\begin{align*}
\text{Scheme II. Dipole Moments (Debye, in Parentheses) of Pentafulvenes} \\
\text{Dipole Moments}
\end{align*}
\]

As noted above, the calculated dipole moments of ketenes agree within limits with available experimental values, being consistently higher by 0.2 D for 6-31G*/6-31G* calculations. For the fulvenes 1, 2b, 2c, and 3b, and the ketene 10, the calculated values are 0.44, 0.01, 0.01, and 0.28 D larger than the ketene experimental values (Table VI, supplementary material). Thus, the calculated values give reasonable agreement with experimental values and with discretion can be used as an aid in the interpretation of the electronic structure of the fulvenones. A detailed study\(^{12b}\) of effects of electron correlation on the calculated dipole moment of pentafulvene (2) revealed that MP2 level calculations gave somewhat poorer agreement with the experimental value than did the HF method, although still higher levels did give quite good agreement. Interestingly, of all the levels of theory examined, none gave good agreement for the dipole moments of both cyclopentadiene and fulvene (2) when the same level of theory was applied to both.\(^{12b}\) Rather fortuitously our calculated value of the dipole moment for fulvene (2) of 0.43 D matched the best of the 19 values obtained at higher levels of theory.\(^{12b}\)

The dipole moments given in Scheme I show a 1.94 D greater value for fulvene 1 compared to 11, whereas the difference in the dipole moments of fulvenone 4 and 10 is 1.52 D. This smaller difference for the ketenes is evidence that the dipolar resonance structure shown for 4 is not as favorable as in the case of 1. Ordinarily vinylketenes have reduced dipole moments. Thus, the experimental dipole moment of vinylketene 17 is 0.4 D less than that of ketene itself, and this is attributed\(^{15b}\) to a contribution from the dipolar resonance structure shown for 17. A similar effect is seen for the 4-membered ring structures 14 and 18. The fact that the dipole moment of 4 is significantly greater than that of the saturated analogue 10, in contrast to the opposite effect with 17 and 18, is further evidence for the unfavorable effect of electron donation to the cyclopropenyl ring.

For pentafulvene (2), there is no evidence for any significant change in the dipole moment due to aromaticity effects, as compared to cyclic nonconjugated and acyclic conjugated analogues (Scheme II). However, for pentafulvenone (5), there is a large decrease of 2.01 D in the dipole moment compared to the nonconjugated analogue 16, consistent with the dipolar resonance structure shown for 5 and opposite to the behavior of triafulvenone (4). As already noted, other conjugated alkenylketenes also show decreases in dipole moments, and these have been interpreted in terms of \(\pi\)-donation from the carbonyl group.\(^{15b}\) Thus, there is strong evidence for significant electron donation to the cyclopentadienyl moiety.

The dipole moment of heptafulvene (3) of 0.49 D (Scheme III) is much less than that of triafulvene (1) and gives no evidence in 3 for the dipolar character that is prominent in 1. The dipole moment of heptafulvenone (6) of 1.30 D is also much less than that of 4.39 D for triafulvenone (4). Comparison of the dipole moment of 6 to those for other polyenylketenes (Scheme III) shows no trends in the results and no firm evidence for dipolar structures involving either aromatic or antiaromatic effects of the cycloheptatrienyl system.

Atomic Charges

As already noted, there are a variety of methods for the calculation of atomic charges, but there is widespread disagreement as to the best method and the validity of the results.\(^{14a}\) This topic is the subject of a different study, but a brief comment on the calculated Mulliken atomic charges is warranted. The detailed list of the charges is given in Table V (supplementary material), and the trends are summarized in Table Va (supplementary material), which lists the net charge on the carbonyl (C=O) group of the fulvenones and the terminal methylene (=CH\(_2\)) of the fulvenones, as well as the most negative charges for these groups found in our recent comprehensive study of the effects of second and third period groups on ketene structures.\(^{5e}\)

These charges show that the most negative carbonyl and methylene groups are \(-0.16\) for triafulvenone (4) and \(-0.26\) triafulvene (1), respectively. These are also more negative than for 25 other ketenes and 25 alkenes, respectively, that we have recently studied,\(^{8}\) in which NaCH\(_2\)=C=O and NaCH\(_2\)=CH\(_2\), with corresponding charges of \(-0.11\) and \(-0.18\), respectively, were the most negative.

The concomitant positive charge accumulation on the cyclopropenyl group is consistent with aromatic character in this moiety and thus supports some \(2\pi\)-electron aromatic character in both the fulvenone and the fulvene.

Bond Lengths

The conclusion was reached by Neuenschwander\(^{13a}\) that the fulvenones "are characterized by typically olefinic properties". A major argument for their lack of aromaticity was the characteristic alternation of bond lengths in the rings.

However, as shown (Chart I), the bond alternation, or difference in the length of the ring bonds, in triafulvenone (4) is more than that of triafulvene by 0.054 \(\AA\), and this can be taken as evidence of lesser aromaticity (or greater antiaromaticity) in the ketene. This is in accord with the negative charge on C\(_5\) of the ketene.
For the pentafulvenone/pentafulvene comparison, there is less alternation by an average value of 0.03 Å in the lengths of the ring bonds for the ketene, indicative of greater aromatic character. Even for heptafulvenone (6), this effect is noticeable, as the average difference in adjacent bond lengths is 0.012 Å greater than for heptafulvene (3). Alternatively, it may be noted that the nominal annular double bonds are shorter and the single bonds longer in the fulvenones 4 and 6 compared to corresponding bonds in fulvenes 1 and 3, indicative of greater antiaromatic character in 4 and 6, while the reverse is true for 5 and 2, indicative of greater aromatic character in 5. While these differences in bond lengths are not great, in every case they are in the direction expected for greater aromaticity/antiaromaticity effects in the fulvenones as compared to the fulvenes.

**Diazocyclopropene (7), Diazocyclopentadiene (8), and Diazocycloheptatriene (9)**

The fulvenones 4-6 are isoelectronic to the diazocyclopolyenes 7-9, and the structures and energies of these latter substrates were also calculated. It is thought that the resonance structure 19 contributes to the overall electronic distribution of diazomethanes, so analogous effects to the fulvenones are expected. A full report on substituent effects in diazomethanes is forthcoming.

\[
\begin{align*}
\text{N=N} & \quad \text{N=N} \\
\text{7} & \quad \text{8} & \quad \text{9} & \quad \text{19}
\end{align*}
\]

Apparently there are no previous theoretical or experimental reports of diazocyclopropene (7).\(^{(17)}\) Entries 17 and 18 (Table II) show major destabilization for 7 attributable to antiaromatic effects. This is summarized in the \(\Delta E\) of \(-16.4\) kcal/mol for eq 8, which illustrates the major destabilization of 7 independent of effects due to the small ring.

\[
\begin{align*}
\text{N=N} & \quad \text{CH}_2 \\
\text{7} & \quad \text{1} & \quad \text{N=N}
\end{align*}
\]

Diazocyclopentadiene (8) has been widely studied experimentally,\(^{(3)}\) but the most recent theoretical study was only at the minimal STO-3G level.\(^{(16)}\) As shown in entries 19 and 20 (Table II), this species is appreciably stabilized, as expected for the operation of aromaticity effects. This stabilization is illustrated by the \(\Delta E\) of 6.6 kcal/mol for eq 9.

\[
\begin{align*}
\text{N=N} & \quad \text{CH}_2 \\
\text{8} & \quad \text{1} & \quad \text{N=N}
\end{align*}
\]

Diazocycloheptatriene (9) is known experimentally,\(^{(5)}\) but the negligible energy change in entry 21 (\(-0.5\) kcal/mol) shows that any antiaromaticity effects in this derivative are completely attenuated.

The calculated bond lengths, which for 8 are within the experimental uncertainties of values recently derived from microwave results,\(^{(10)}\) give further evidence for antiaromatic character in 7 and aromatic character in 8. Thus, as shown below for 7, the \(\text{C=N}\) bond length is shorter and the \(\text{N=N}\) bond length is longer compared to 20, whereas for 8 the \(\text{C=N}\) bond length is longer and the \(\text{N=N}\) bond length is shorter compared to 21 or 22. The differences in the \(\text{C=N}\) and \(\text{N=N}\) bond lengths between 7 and 8 are 0.073 and 0.056 Å, respectively. These trends are consistent with a greater contribution from the dipolar resonance structure 19 and aromatic character for 8 and a lesser contribution for 7. The patterns in the \(\text{C-C}\) bond lengths for 7-9 correspond to those of 4-6 (Chart I), respectively, consistent with antiaromatic character in 7 and aromatic character in 8.

The net Mulliken charge on the diazo group is \(-0.44\) in 7, \(-0.22\) in 20, \(-0.16\) in 8, and \(-0.23\) in 9, again in agreement with a greater contribution from the dipolar structure 19 for 8 and a lesser contribution in 7 and 9.

In summary, the calculated structures and energies of the fulvenones 4-6 indicate the influence of these species of simple Hückel aromatic effects, in that triafulvenone (4), pentafulvenone (5), and heptafulvenone (6) have the character of 4-, 6-, and 8-\(\pi\)-electron systems, respectively. Antiaromatic destabilization of 4 and 6 and aromatic stabilization of 5 is most prominent in isodemic energy comparisons but is also manifested in dipole moment, atomic charge, and bond length comparisons. Similar behavior is seen for diazocyclopropene (7), diazocyclopentadiene (8), and some fluorinated analogues.

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**Supplementary Material Available:** Detailed energies and dipole moments (Table III), 6-31G*/6-31G* bond lengths (Table IV), Mulliken charges (Table V), experimental and calculated bond distances (Table VI), single-point calculated total energies (Table VII), and isodemic energy changes (Table VIII) (22 pages). Ordering information is given on any current masthead page.