corporated into DNA triple helices.

The electronic and conformational properties of MEC versus CYT at the isolated nucleoside level deserve careful consideration since both protonated species are cationic and differ only by the presence or absence of a methyl group at C5. In previous studies, it has been demonstrated that the methyl group at C5 improved the binding of MEC relative to CYT when incorporated into DNA duplex systems because of increased base stacking energy.[16] This increased base stacking energy which accompanies cytosine methylation results in an improved enthalpy, $\Delta H°$, in duplex DNA and may underlie the improved stability of MEC-substituted triplex DNA complexes. It is reasonable to consider that altered intramolecular and intermolecular dielectric shielding of the positive charge of the proton at N3 may be an important feature of MEC substitution in DNA triple helices. An alteration in dielectric shielding induced by the C5 methyl group may result in a more favorable charge polarization of the MEC molecule to facilitate either Hoogsteen pairing or base stacking within the DNA triplex. We have previously noted significant changes in charge density in the region of the C5 methyl group in MEC relative to the hydrogen atom at C5 in CYT.[16] We are presently investigating whether there are any significant differences in the electronic factors between CYT and MEC which may help to develop a clear explanation of the improved thermal stability of MEC-substituted oligomers in DNA triple helices.

The utility of applying ab initio quantum mechanics and statistical mechanical methods in the study of microscopic and macroscopic properties of nucleic acid systems appears to have some utility for future research. The combined application of experimental data with numerical simulation permits semiquantitative and, in some instances, quantitative predictions which can be tested and further refined by experiment. The combined use of experimental and theoretical data, as in the present work, improves the ability to characterize key molecular mechanisms of interest in a useful and complementary manner. This integrated approach makes it possible to develop and refine hypotheses which can be tested in the laboratory. It should be clear from this work that laboratory data are essential to develop, calibrate, validate, and improve numerical models in a recursive, stepwise manner. The key role of numerical simulations will be to provide observations which should be useful in experimental design and productivity by proposing increasingly accurate estimations of physicochemical properties with reasonable confidence.

Acknowledgment. All calculations were carried out on a GRAY Y-MP 8/64 in Eagan, MN. This research was supported by academic grants from Cray Research (K-GAHM-XX-531-2-99 and K-531-1-99) and from Sterling Drug Inc.

Fulvenones and Isoelectronic Diazocyclopolyenes: Theoretical Studies of Structures and Stabilization

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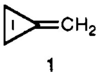
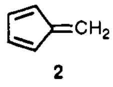
Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1. Received November 14, 1991

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 pentafulvene (**2**). 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. Diazocyclopropene (**7**), diazocyclopentadiene (**8**), and diazocycloheptatriene (**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.[1a–h] The question of the aromatic/antiaromatic character of these and similar rings has attracted particular attention.[1]



1



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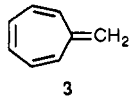

3

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, $\mathbf{5}^{3-5}$ and $\mathbf{6}^{6}$ have been studied

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[1] (a) Neuenschwander, N. Fulvenes. In *The Chemistry of Functional Groups. Supplement A. The Chemistry of Double-bonded Functional Groups.* Patai, S., Ed.; Wiley, New York, 1989; Vol. 2, Parts 1 and 2. (b) Yates, P. *Adv. Alicycl. Chem.* **1968**, *2*, 59–184. (c) Becker, G. Triafulvenes. *Houben-Weyl, Method. Org. Chem.* **1985**, *5/2c*, 476–478. (d) Zeller, K. P. Pentafulvenes. *Ibid.* **1985**, *5/2c*, 504–684. (e) Asao, T.; Oda, M. Heptafulvenes. *Ibid.* **1985**, *5/2c*, 768–780. (f) Bergmann, E. D. *Chem. Rev.* **1968**, *68*, 41–84. (g) Bachrach, S. M.; Liu, M. *J. Phys. Org. Chem.* **1991**, *4*, 242–250. (h) Jug, K.; Koster, A. M. *J. Phys. Org. Chem.* **1991**, *4*, 163–169. (i) Byun, Y.; Saebo, S.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 3689–3696.

[2] Alternative names are cyclopropylideneketene (**4**), cyclopentylidieneketene (**5**), and cycloheptylideneketene (**6**). Chemical Abstracts names are methanone, 2-cyclopropen-1-ylidone (**4**); methanone, 2,4-cyclopentadien-1-ylidone (**5**), and methanone, 2,4,6-cycloheptatrien-1-ylidone (**6**).

[3] (a) Süs, O. *Liebigs Ann. Chem.* **1944**, *556*, 65–85. (b) Urwyler, B.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 790–791. (c) Mamer, O. A.; Rutherford, K. G.; Seidewand, R. J. *Can. J. Chem.* **1974**, *52*, 1983–1987. (d) Bloch, R. *Tetrahedron Lett.* **1978**, 1071–1072. (e) Schulz, R.; Schweig, A. *Ibid.* **1979**, 59–62. (f) Schweig, A.; Zittlau, W. *Chem. Phys.* **1986**, *103*, 375–382. (g) Schulz, R.; Schweig, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 509–511. (h) Baird, M. S.; Dunkin, I. R.; Hacker, N.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 5190–5195. (i) Chapman, O. L. *Pure Appl. Chem.* **1979**, *51*, 331–339. (j) Clinging, R.; Dean, F. M.; Mitchell, G. H. *Tetrahedron* **1974**, *30*, 4065–4067. (k) Tanigaki, K.; Ebbesen, T. W. *J. Phys. Chem.* **1989**, *93*, 4531–4536.

[4] (a) Thompson, L. F.; Willson, C. G.; Bowden, M. J. S. *Introduction to Microlithography*; American Chemical Society: Washington, DC, 1989. (b) De Forest, W. S. *Photoresist: Materials and Processes*; McGraw-Hill: New York, 1975; pp 132–162.

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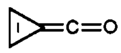
experimentally, as well as the benzo derivatives of **5**.[4,5] By contrast, there have apparently been no experimental studies of **4**,[7a] although there are theoretical studies of its structure[7b] and reaction with protons and H_2O.[7c]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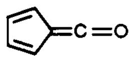
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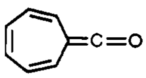
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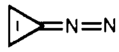
Derivatives of compound **5** have major practical applications in photoresists[4] and have been the object of many experimental studies,[4,5] while **6** has been generated and utilized as a synthetic intermediate[6] but has not been studied theoretically. Despite the possible influence of aromaticity/antiaromaticity 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**, isoelectronic to **4**–**6**, respectively, are of similar interest and have also been examined.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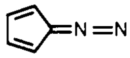
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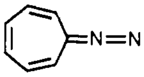
9

Ketenes have recently been of interest to us[8] and are also being actively examined by others both experimentally[9] and theoretically.[7,10] We have found that ab initio calculations of the structures and energies of ketenes[8a,e] and diazo compounds[8g] 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,[7b,c] 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 fulvenes are available.

Methodology and Results

Calculations were carried out using the GAUSSIAN 88[11a] package implemented by the MONSTERGAUSS program[11b] using Apollo DN10000 and IBM 6000 minicomputers. Gradient techniques using the Optimally Conditioned method[11c] 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,[11c] 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, divinylketene, **6**, **9**, and **14**, 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**[12b,f] and **2**.[12g]

Atomic charges were calculated from the Mulliken population analysis[11c] 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,[11d] the natural population analysis,[11e] and generalized atomic polar tensors (GAPT).[11f] However, Bader's method itself has been criticized,[11g] and the GAPT method is admitted[11f] 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 greatly between the values calculated with the 3-21G and 6-31G* basis sets. The same behavior has been found for ketenes[8e] and diazomethanes[8g] 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 ΔE values (kcal/mol) of −17.3, −14.2, −13.9, and −13.0, respectively, for entry 1 and −23.0, −25.3, −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.

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(10) (a) Bernardi, F.; Bottoni, A.; Robb, M. A.; Venturini, A. *J. Am. Chem. Soc.* **1990**, *112*, 2106–2114. (b) Wang, X.; Houk, K. N. *Ibid.* **1990**, *112*, 1754–1755. (c) Seidl, E. T.; Schaeffer, H. F., III. *Ibid.* **1991**, *113*, 5195–5200. (d) Valenti, E.; Pericas, M. A.; Moyano, A. *J. Org. Chem.* **1990**, *55*, 3582–3593. (e) Nguyen, M. T.; Ha, T.; More O'Ferrall, R. A. *Ibid.* **1990**, *55*, 3251–3256.

(11) (a) Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1988. (b) Peterson, M. R.; Poirier, R. A. Department of Chemistry, University of Toronto. (c) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986. (d) Bader, R. F. W. *Acc. Chem. Res.* **1975**, *8*, 34–40. (e) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735–746. (f) Cioslowski, J. *J. Am. Chem. Soc.* **1989**, *111*, 8333–8336. (g) Perrin, C. L. *Ibid.* **1991**, *113*, 2865–2868.

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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

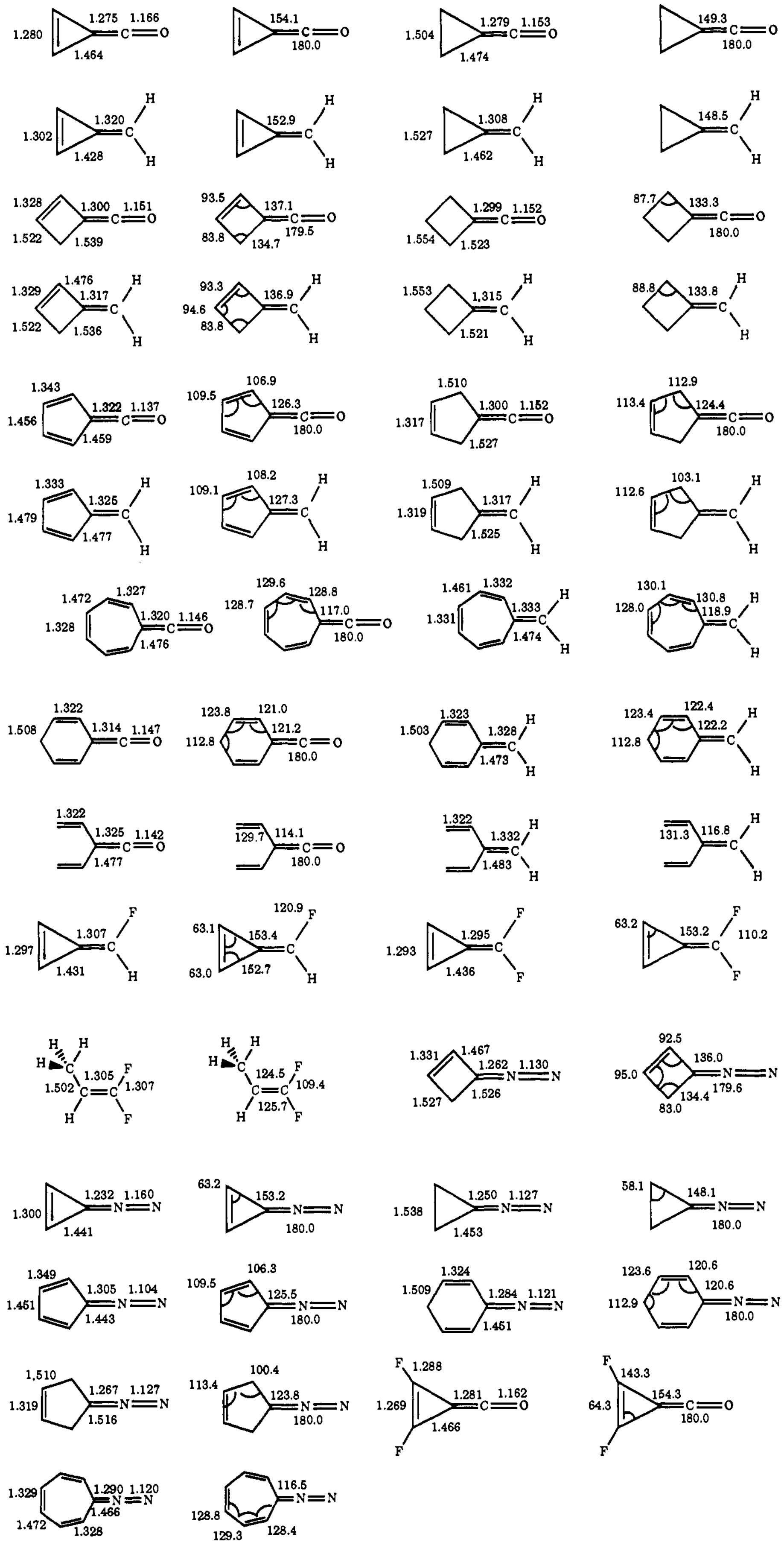
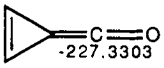
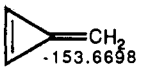
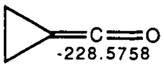
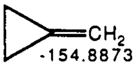
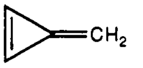
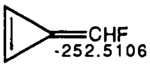
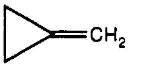
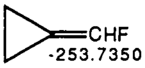
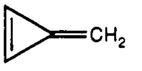
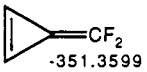
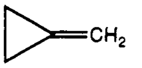
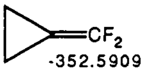
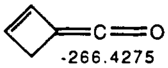
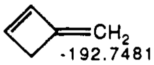
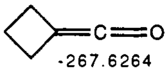
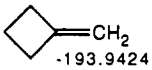
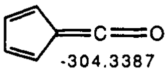
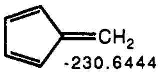
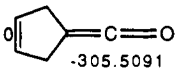
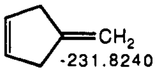
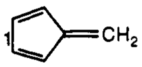
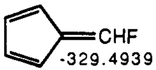
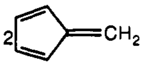
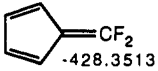
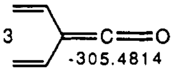
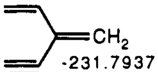
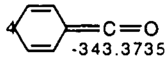
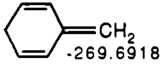
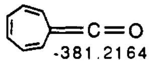
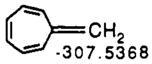
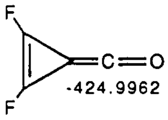
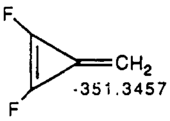
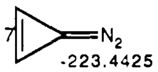
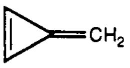
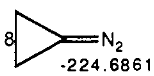
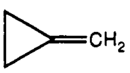
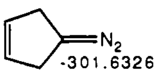
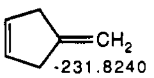
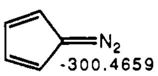
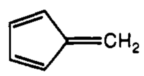
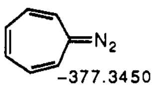
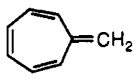


Table II. Energies (hartrees) (6-31G*//6-31G*) for Fulvenones and Fulvenes and Stabilization Energies (ΔE, kcal/mol) for Some Isodesmic Reactions of Fulvenones

						3-21G	6-31G*
1	 -227.3303	+ $CH_3CH{=}CH_2$ -117.0715	→	 -153.6698	+ $CH_3CH{=}C{=}O$ -190.7592	-13.2	-17.1
2	 -228.5758	+ $CH_3CH{=}CH_2$	→	 -154.8873	+ $CH_3CH{=}C{=}O$	2.4	0.5
3		+ $CH_3CH{=}CHF$ -215.9215 (*Z*) -215.9205 (*E*)	→	 -252.5106	+ $CH_3CH{=}CH_2$	5.4	5.7
4		+ $CH_3CH{=}CHF$	→	 -253.7350	+ $CH_3CH{=}CH_2$	1.7	1.4
5		+ $CH_3CH{=}CF_2$ -314.7780	→	 -351.3599	+ $CH_3CH{=}CH_2$	8.6	10.3
6		+ $CH_3CH{=}CF_2$	→	 -352.5909	+ $CH_3CH{=}CH_2$	1.5	1.9
7	 -266.4275	+ $CH_3CH{=}CH_2$	→	 -192.7481	+ $CH_3CH{=}C{=}O$	-3.4	-5.2
8	 -267.6264	+ $CH_3CH{=}CH_2$	→	 -193.9424	+ $CH_3CH{=}C{=}O$	-1.2	-2.3
9	 -304.3387	+ $CH_3CH{=}CH_2$	→	 -230.6444	+ $CH_3CH{=}C{=}O$	5.1	4.1
10	 -305.5091	+ $CH_3CH{=}CH_2$	→	 -231.8240	+ $CH_3CH{=}C{=}O$	-1.1	-1.6
11		+ $CH_3CH{=}CHF$	→	 -329.4939	+ $CH_3CH{=}CH_2$	0.3	0.3
12		+ $CH_3CH{=}CF_2$	→	 -428.3513	+ $CH_3CH{=}CH_2$	-0.8	-0.2
13	 -305.4814	+ $CH_3CH{=}CH_2$	→	 -231.7937	+ $CH_3CH{=}CH_2$	-0.2	0.0
14	 -343.3735	+ $CH_3CH{=}CH_2$	→	 -269.6918	+ $CH_3CH{=}C{=}O$	-3.2	-3.8
15	 -381.2164	+ $CH_3CH{=}CH_2$	→	 -307.5368	+ $CH_3CH{=}C{=}O$	-5.2	-5.1
16	 -424.9962	+ $CH_3CH{=}CH_2$	→	 -351.3457	+ $CH_3CH{=}C{=}O$	-19.7	-23.4
17	 -223.4425	+ $CH_3CH{=}CH_2$	→		+ $CH_3CH{=}N_2$ -186.8805	-15.1	-22.8
18	 -224.6861	+ $CH_3CH{=}CH_2$	→		+ $CH_3CH{=}N_2$	-2.5	-6.4
19	 -301.6326	+ $CH_3CH{=}CH_2$	→	 -231.8240	+ $CH_3CH{=}N_2$	1.2	-0.3
20	 -300.4659	+ $CH_3CH{=}CH_2$	→		+ $CH_3CH{=}N_2$	11.6	7.8
21	 -377.3450	+ $CH_3CH{=}CH_2$	→		+ $CH_3CH{=}N_2$	1.4	-0.5

A comparison of experimental bond distances[12] for the fulvenes **1–3** with the calculated (6-31G*) values is 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.[8e] It was found[12b] that the MP2/6-31G* basis set including electron correlation gave a calculated geometry for **1** 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.[8e]

Despite two reports of microwave studies of cyclopropylidenemethanone (**10**),[12a,c] no experimental geometries of cycloalkylidene ketenes or fulvenones have been reported.

Energies

Recently[8e] 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

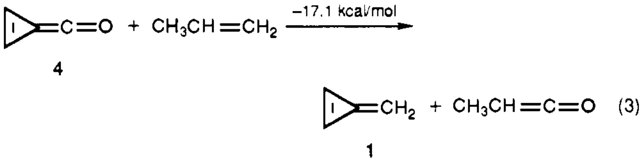
$$RCH{=}C{=}O + CH_3CH{=}CH_2 \rightarrow CH_3CH{=}C{=}O + RCH{=}CH_2 \quad (1)$$

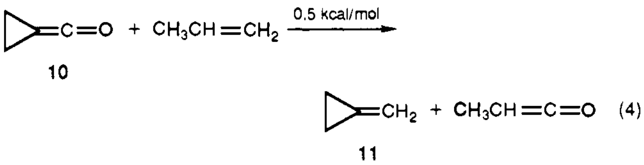
methods using the 6-31G*//6-31G* basis set. It was found that ΔE for this reaction could be correlated by substituent-group electronegativity parameters X_{BE} as reported by Boyd and Edgecombe.[13] Further analysis of the results suggested that ketenes are stabilized by π-acceptor substituents and destablized by π-donors and by σ-donors.[8e]

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.

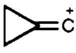
$$R_2C{=}C{=}O + CH_3CH{=}CH_2 \rightarrow CH_3CH{=}C{=}O + R_2C{=}CH_2 \quad (2)$$

Ketenes are negatively charged on C_β,[8e] and this leads to the prediction that triafulvenone may be destabilized by antiaromatic effects. The calculated ΔE for the isodesmic reaction of triafulvenone (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, for the saturated analogue **10** shows a net stabilization of 0.5 kcal/mol (eq 4).



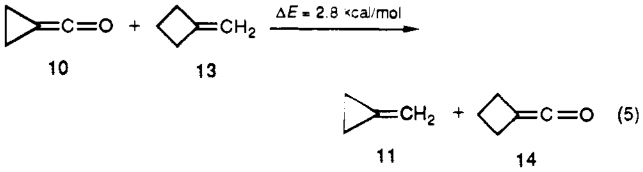


The small net energy change shown in eq 4 may result from a combination of opposing stabilizing and destabilizing effects on the ketene **10**. Thus, the cyclopropyl ring is σ-electron-withdrawing by hybridization effects,[14] and electronegative groups are destabilizing as ketene substituents.[8e] However, to the extent that **10** has the character of a cyclopropyl anion, a stabilized species,[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 σ-bonds of the cyclopropyl to the vacant p orbital of the vinyl cation.[14c]

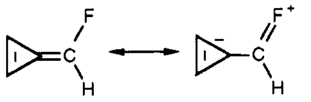


12

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.

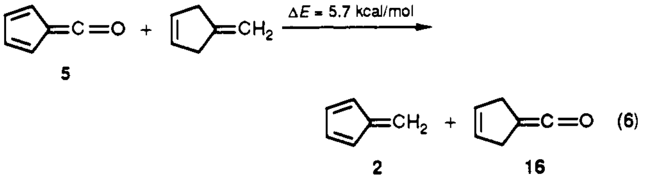


To probe the origin of the destabilizing effect of the carbonyl group of **4** compared to other electronegative substituents, the effects of fluorine have also been examined.[15a] There are only small effects on methylenecyclopropane (**11**), with destabilizations of 1.4 and 1.9 kcal/mol for one and two fluorines, respectively (entries 4 and 6, Table II). Thus, effects due to electronegative substituents on the methylenecyclopropane structure appear to be small. However, fluorines 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 π-donor ability. The latter effect leading to resonance structure **15** would result in 4π-electron antiaromatic destabilization, and evidently this causes the large net destabilization.

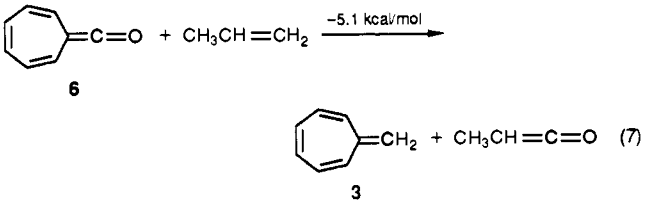


15

Pentafulvenone (**5**) itself is found from the isodesmic reaction to be stabilized by 4.1 kcal/mol relative to methylketene (entry 9, Table II) or by 5.7 kcal/mol by the comparison of eq 6. Nonaromatic dienylketenes show no stabilizing effects (Table II, entries 13 and 14). There are no significant energetic effects of fluorination on the pentafulvene structure (entries 11 and 12, Table II).



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**.



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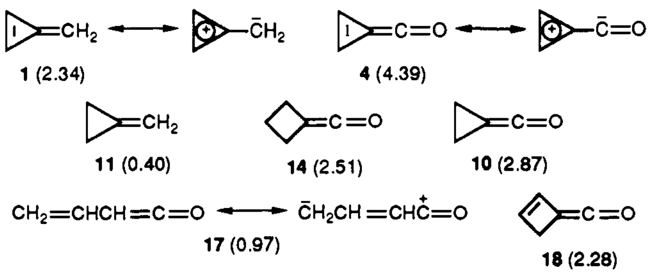
(13) Boyd, R. J.; Edgecombe, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 4182–4186.

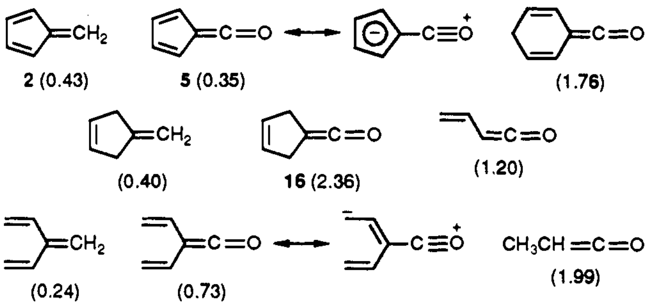
(14) (a) Tidwell, T. T. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: London, 1987. (b) Walborsky, H. In *Cyclopropane Derived Reactive Intermediates*; Patai, S., Ed.; Wiley: London, 1990. (c) Hanack, M. *Acc. Chem. Res.* **1976**, *9*, 364–371.

(15) (a) For a recent study of the effects of fluorine substitution on the aromaticity of cyclopropenone, see: Jacobs, C. A.; Brahms, J. C.; Dailey, W. P.; Beran, K.; Harmony, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 115–121. (b) Brown, R. D.; Godfrey, P. D.; Woodruff, M. *Aust. J. Chem.* **1979**, *32*, 2103–2109.

Scheme I. Dipole Moments (Debye, in Parentheses) of Triafulvenes and Analogues



Scheme II. Dipole Moments (Debye, in Parentheses) of Pentafulvenes



Scheme III. Dipole Moments (Debye, in Parentheses) of Heptafulvenes

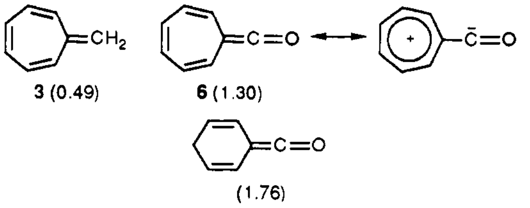
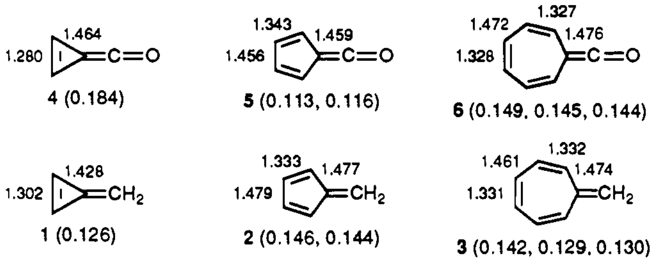


Chart I. Calculated Intraring C–C Bond Lengths (Å) and Differences (Parentheses) between Adjacent Bond Lengths



Dipole Moments

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.[8e] For the fulvenes **1**,[12b] **2**,[12b] and **3**[12c] and the ketene **10**,[12a] 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[12h] 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.[12h] 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.[12h]

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 π-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.[11d-g] 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 fulvenes, 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.[8e]

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,[8e] in which $NaCH{=}C{=}O$ and $NaCH{=}CH_2$, 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 2π-electron aromatic character in both the fulvenone and the fulvene.

Bond Lengths

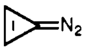
The conclusion was reached by Neuenschwander[1a] that the fulvenes "are characterized by typically olefinic properties". A major argument for their lack of aromaticity was the characteristic alternation of bond lengths in the rings.

However, as shown (Chart I), the bond alternation, or difference in the length of the ring bonds, in triafulvelenone (**4**) is more than that of triafulvalene by 0.054 Å, 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_β of the ketene.

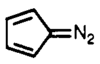
For the pentafulvenone/pentafulvene comparison, there is less alternation by an average value of 0.03 Å in the lengths of the ring bonds for the ketene, indicative of greater aromatic character. Even for heptafulvenone (**6**), this effect is noticeable, as the average difference in adjacent bond lengths 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[16] 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.[8g]



7



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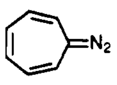

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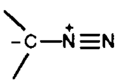
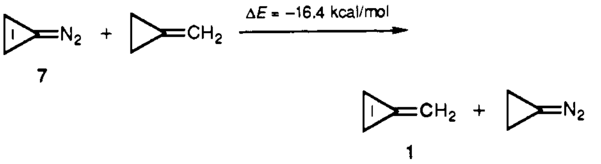


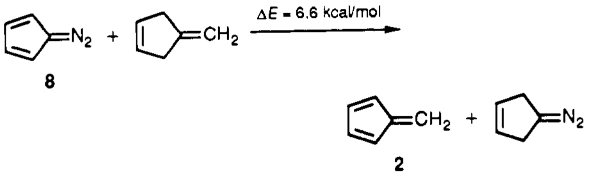
19

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 ΔE of −16.4 kcal/mol for eq 8, which illustrates the major destabilization of **7** independent of effects due to the small ring.



(8)

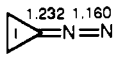
Diazocyclopentadiene (**8**) has been widely studied experimentally,[3h,18a,b] but the most recent theoretical study was only at the minimal STO-3G level.[18c] As shown in entries 19 and 20 (Table II), this species is appreciably stabilized, as expected for the operation of aromaticity effects. This stabilization is illustrated by the ΔE of 6.6 kcal/mol for eq 9.



(9)

Diazocycloheptatriene (**9**) is known experimentally,[6i] 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,[18b] give further evidence for antiaromatic character in **7** and aromatic character in **8**. Thus, as shown below for **7**, the C═N bond length is shorter and the N═N bond length is longer compared to **20**, whereas for **8** the C═N bond length is longer and the N═N bond length is shorter compared to **21** or **22**. The differences in the C═N and 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 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**.



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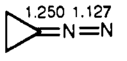

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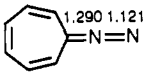

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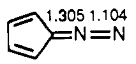

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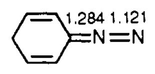

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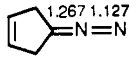

22

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 on these species of simple Huckel aromatic effects, in that triafulvenone (**4**), pentafulvenone (**5**), and heptafulvenone (**6**) have the character of 4-, 6-, and 8π-electron systems, respectively. Antiaromatic destabilization of **4** and **6** and aromatic stabilization of **5** is most prominent in isodesmic 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.

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[16] (a) Regitz, M.; Maas, G. *Diazo Compounds. Properties and Synthesis*; Academic: New York, 1986. (b) Moffat, J. B. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: New York, 1978. (c) Moffat, J. B. *J. Mol. Struct.* **1979**, *52*, 277–280.

[17] Extensive but unsuccessful efforts to prepare the diphenyl derivative of 7 have been described: Jones, W. M.; Stowe, M. E.; Wells, E. E., Jr.; Lester, E. W. *J. Am. Chem. Soc.* **1968**, *90*, 1849–1859.

[18] (a) Doering, W. v. E.; DePuy, C. H. *J. Am. Chem. Soc.* **1953**, *75*, 5955–5957. (b) Sakaizumi, T.; Fukuda, S.; Ohashi, O.; Yamaguchi, I. *J. Mol. Spectrosc.* **1990**, *141*, 325–333. (c) Moffat, J. B. *J. Phys. Chem.* **1978**, *82*, 1083–1087.