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Comparative Cumulene Substituent Effects: Ketenes, Allenes, Diazomethanes, Diazirines, and Cyclopropenes by *ab Initio* Molecular Orbital Calculations

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Ab initio calculations of the effect of substituents on the structures and energies of ketenes (**1**), diazomethanes (**3**), diazirines (**4**), allenes (**5**), and cyclopropenes (**6**) reveal that the isodesmic substituent stabilization energies of **1**, **3**, and **5** relative to alkenes are correlated with group electronegativities with slopes of −15.1, −10.6, and −5.8, respectively, at the HF/6-31G*+ZPVE//HF/6-31G* level, corresponding to a successive decrease in polar character of the cumulenes in this order. Isomerization energies of **3** to **4** show that the relative stabilities of substituted diazomethanes and diazirines are dominated by the stabilization of diazomethanes by electropositive substituents. The energetics of the isomerization of allenes **5** to cyclopropenes **6** are affected by a general greater stability of allenes due to the ring strain of cyclopropenes, a greater stabilization of allenes by electropositive substituents, and aromaticity/antiaromaticity effects in which cyclopropenes are favored by electronegative substituents and disfavored by electropositive substituents. A comparison of charges calculated by the Mulliken, Natural Bond Orbital (NBO), and Bader methods reveals similar trends in the charges from all three methods, with good correlations between the Mulliken and NBO charges. The best correlations of charges with substituent electronegativity are found for the NBO-derived charges. The Bader charges do not correlate well with Mulliken and NBO charges, nor with electronegativity, and give very large absolute atomic charges in many cases. The calculated cumulene IR asymmetric stretching vibrations are correlated with measured values for ketenes and allenes, but for diazomethanes the calculations are of limited diagnostic utility.

The systematic study by *ab initio* molecular orbital calculations of substituent effects on the structure and energetics of the different classes of the major functional groups in organic compounds has been pursued by many groups in recent years.[1−5] These studies include alkanes,[2a] alkenes,[1b,2a,3c−e] alkynes,[3c−e] allenes,[3a,b] 1,3-dienes,[2b,c] cyclopropanes,[1g,2a,3c,e,g] diazo compounds and diazirines,[4] carbonyl compounds,[2d] carbocations,[1d] carbanions,[1e] and organolithium compounds.[1c] We have been particularly interested in cumulene systems[5] and have found that *ab initio* calculations have been quite informative for the understanding of substituent effects, structures, and reactivities of ketenes,[5a] fulvenones,[5b] diazomethanes and the isomeric diazirines,[5c] bisketenes,[5d,e] isocyanates,[5f] and imines.[5f]

These studies have utilized isodesmic reactions as in eq 1 to compare the effect of substituents on ketenes **1** to those on alkenes **2**, with CH_3 as a reference substituent.[5a] This approach has been widely used[1a] and offers the advantage that the effect of the substituent on the property in question is isolated and systematic errors are minimized. We have also found that the group electronegativities χ_{BE}, as introduced by Boyd, Boyd, and Edgecombe,[6] give good correlations of the stabilization energies (SE) for many substituents derived from eq1.

$$\underset{\mathbf{1}}{RCH{=}C{=}O} + CH_3CH{=}CH_2 \xrightarrow[\Delta E]{SE\,=} CH_3CH{=}C{=}O + \underset{\mathbf{2}}{RCH{=}CH_2} \qquad (1)$$

The study by theoretical methods of diazomethanes **3** and diazirines **4** has been actively pursued by many groups,[4] but there has been considerable uncertainty as

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[1] (a) Schleyer, P. v. R. *Pure Appl. Chem.* **1987**, *59*, 1647−1660. (b) Heinrich, N.; Koch, W.; Frenking, G.; Schwarz, H. *J. Am. Chem. Soc.* **1986**, *108*, 593−600. (c) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909-5916. (d) White, J. C.; Cave, R. J.; Davidson, E. R. *J. Am. Chem. Soc.* **1988**, *110*, 6308−6314. (e) Bernardi, F.; Bottoni, A.; Valli, G. S.; Venturini, A. *Gazz. Chim. Ital.* **1990**, *120*, 301−307. (f) Replogle, E. S.; Trucks, G. W.; Staley, S. W. *J. Phys. Chem.* **1991**, *95*, 6908−6912. (g) Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 4412−4419.

[2] (a) Wiberg, K. B.; Laidig, K. E. *J. Org. Chem.* **1992**, *57*, 5092−5101. (b) Wiberg, K. B.; Rosenberg, R. E.; Rablen, P. R. *J. Am. Chem. Soc.* **1991**, *113*, 2890−2898. (c) Wiberg, K. B.; Rosenberg, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1509−1519. (d) Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644−8654. (e) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 9234−9242.

[3] (a) Furet, P.; Machta, R. L.; Fuchs, R. *J. Phys. Chem.* **1986**, *90*, 5571−5573. (b) Lambert, C.; Schleyer, P. v. R.; Würthwein, E.-U. *J. Org. Chem.* **1993**, *58*, 6377−6389. (c) Greenberg, A.; Stevenson, T. A. *J. Am. Chem. Soc.* **1985**, *107*, 3488−3494. (d) Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 6814−6825. (e) Lien, M. H.; Hopkinson, A. C. *J. Mol. Struct. (Theochem)* **1987**, *149*, 139−151. (f) Boyaraskaya, I. A.; Baidin, V. N.; Domnin, I. N. *Zh. Org. Khim.* **1990**, *26*, 2303−2312. (g) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3811−3819.

[4] (a) Müller-Remmers, P. L.; Jug, K. *J. Am. Chem. Soc.* **1985**, *107*, 7275-7284. (b) Wang, F.; Winnik, M. A.; Peterson, M. P.; Csizmadia, I. G. *J. Mol. Struct.* **1991**, *232*, 203−210. (c) Boldyrev, A. I.; Schleyer, P. v. R.; Higgins, D.; Thomson, C.; Kramarenko, S. S. *J. Comput. Chem.* **1992**, *13*, 1066−1078. (d) Thomson, C; Glidewell, C. *J. Comput. Chem.* **1983**, *4*, 1−8. (e) Kahn, S. D.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1871−1873. (f) Guimon, C.; Khayar, S.; Gracian, F.; Begtrup, M.; Pfister-Guillouzo, G. *Chem. Phys.* **1989**, *138*, 157−171. (g) Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1991**, *113*, 1878−1884. (h) Moffat, J.B. *J. Phys. Chem.* **1978**, *82*, 1083−1087. (i) Moffat, J. B. *J. Mol. Struct.* **1979**, *52*, 277−280. (j) Goodman, J. M.; James, J. J.; Whiting, A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 109−116.

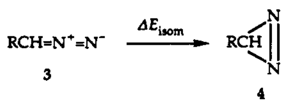
[5] (a) Gong, L.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1991**, *113*, 6021−6028. (b) McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1992**, *114*, 5263−5269. (c) McAllister M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1992**, *114*, 6553-6555. (d) Zhao, D.-c.; Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1993**, *115*, 10097−10103. (e) McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.*, in press. (f) McAllister, M. A.; Tidwell, T. T. *J. Chem. Soc., Perkin Trans. 2,* submitted for publication. (g) McAllister, M. A.; Tidwell, T. T. *Can. J. Chem.* **1994**, *72*, 882−887.

[6] (a) Boyd, R. J.; Edgecombe, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 4182-4186. (b) Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652−1655.

0022-3263/94/1959-4506$04.50/0

to the comparative effects of substituents on these two species. Therefore we have undertaken a study of the structures and energies of these two series to determine isodesmic stabilization energies according to eq 2 and isomerization energies ΔE_{is} according to eq 3 to reveal the comparative substituent effects in the two families. As discussed below, the charge distribution in diazo compounds may be represented by several resonance structures, and the formalism shown in **3** does not imply that this is the major contributor.

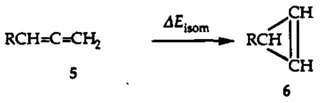
$$\underset{\mathbf{3}}{RCH{=}N^{+}{=}N^{-}} + CH_3CH{=}CH_2 \xrightarrow[= \Delta E]{SE} CH_3CH{=}N^{+}{=}N^{-} + RCH{=}CH_2 \quad (2)$$



3 **4** (3)

The question arises as to whether some of the properties of the diazirines **4** may be affected by the nature of the small ring, with a nontypical electronic arrangement and conjugative properties. To better understand these effects, we have also carried out calculations on allenes **5** and the isomeric cyclopropenes **6**. There have been previous theoretical studies of substituent effects on allenes[3a,b] and cyclopropenes,[3d,e] but these have involved rather small sets of substituents and lower levels of theory and have not included comparisons of the different families. Comparative results are available for cyclopropanes, which have recently been examined at a high level.[2a] We have now calculated ΔE_{is} for allenes to cyclopropenes according to eq 5.

$$\underset{\mathbf{5}}{RCH{=}C{=}CH_2} + CH_3CH{=}CH_2 \xrightarrow[= \Delta E]{SE} CH_3CH{=}C{=}CH_2 + RCH{=}CH_2 \quad (4)$$



5 **6** (5)

Included in this report are an extension of our previous study of ketenes[5a] to test if the inclusion of electron correlation and zero point vibrational energy (ZPVE) affect the previous conclusions, a full discussion on diazomethanes and diazirines,[5c] and a comparison of the calculation of atomic charges by different methods.[7]

The question of whether atomic charges can be meaningfully obtained by molecular orbital calculations has been of continued interest. The most widely used (and criticized) method of electron population analysis is that due to Mulliken[7a] and others are Natural Population Analysis,[7b] the zero-flux surface partitioning of Bader, or Bader Population Analysis,[7c] and others.[7d] There has been a lively debate over the correctness of these methods,[7e-g] and this discussion is by no means settled. However this topic has been clouded by a shortage of comparative data for charges calculated by these different methods for a well-defined group of substrates and so these charges have been calculated by some of these methods for the compounds examined in this study.

Results

The *ab initio* molecular orbital calculations were carried out using the Gaussian 90 and Gaussian 92 series of programs[8a] on Hewlett Packard 9000−750 and IBM RS/6000-530 minicomputers. All geometries are gradient optimized using the standard split valence HF/6-31G* basis set,[8b,c] with the Berny optimizer with no geometrical constraints.[8b] The orders (number of negative diagonal elements of the Hessian matrix of all critical points) were determined at the HF/6-31G* level by analytical differentiation of the restricted Hartree−Fock wave function. Geometries which were optimized at the MP2/6-31G* level were also order checked at that level. The frozen core approximation was not used.

In Table 1 are compiled MP2/6-31G*//MP2/6-31G* calculated energies for substituted ketenes and alkenes, zero point vibrational energies (ZPVE) at this level scaled by 0.95, and ΔE values (including ZPVE) for the isodesmic reaction of eq 1 at this level, or, if these are not available, ΔE values at the HF/6-31G*//HF/6-31G* level (including ZPVE). Also included are HF/6-31G*//HF/6-31G* energies and calculated zero point vibrational energies (ZPVE, scaled by 0.9) for diazomethanes, diazirines, allenes, and cyclopropenes and ΔE values for the isodesmic reactions of eqs 2 and 4 including ZPVE, as well as values of ΔE_{is} for the isomerization reactions of eqs 3 and 5, including ZPVE. These scaling factors are the optimized values from a study of ketene stretch-

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(7) (a) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833−1840; 1841−1846; 2338−2341; 2343−2346. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735−746. (c) Bader, R. F. W. *Atoms in Molecules-A Quantum Theory;* Oxford Press: New York, 1990. (d) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142−4145. (e) Perrin, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 2865−2868. (f) Laidig, K. E. *J. Am. Chem. Soc.* **1992**, *114*, 7912−7913. (g) Gati, C.; Fantucci, P. *J. Phys. Chem.* **1993**, *97*, 11677−11680. (h) AIMPAC: 1990 version provided by R. F. W. Bader, McMaster University, Hamilton, Ontario, Canada. (i) Birney, D. M. *J. Org. Chem.* **1994**, *59*, 2557−2564.

(8) (a) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M.W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R.L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Gaussian, Inc.: Pittsburgh, PA, 1992. (b) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley: New York, 1986. (c) Hariharan, P. C.; Pople, J. A. *Theoret. Chim. Acta* **1973**, *28*, 213−222. (d) Houk, K. N.; Gustafson, S. M.; Black, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 8565−8572.

(9) (a) Duncan, J. L.; Munro, B. *J. Mol. Struct.* **1987**, *161*, 311−319. (b) Brown, R. D.; Godfrey, P. D.; McNaughton, D.; Pierlot, A. P.; Taylor, W. H. *J. Mol. Spect.* **1990**, *140*, 340−352. (c) Bak, B.; Christiansen, J. J.; Kunstmann, K.; Nygaard, L.; Rastrup-Anderson, J. *J. Chem. Phys.* **1966**, *45*, 883−887. (d) Brown, R.D.; Godfrey, P. D.; Wiedenmann, K. H. *J. Mol. Spect.* **1989**, *136*, 241−249. (e) Gerry, M. C. L.; Lewis-Bevan, W.; Westwood, N. P. C. *J. Chem. Phys.* **1983**, *79*, 4655−4663. (f) Hahn, M.; Bodenseh, H. In *Tenth Colloquium on High Resolution Molecular Spectroscopy*; Dijon, 1987; M16.

(10) (a) Hirota, E.; Matsumura, C. *J. Chem. Phys.* **1973**, *59*, 3038−3042. (b) Ogata, T. *J. Phys. Chem.* **1992**, *96*, 2089−2091. (c) Ogata, T; Fujii, K.; Yoshikawa, M.; Hirota, F. *J. Am. Chem. Soc.* **1987**, *109*, 7639−7641. (d) Bijen, J. M. J.M.; Derissen, J. L. *J. Mol. Struct.* **1972**, *14*, 229−233. (e) Derissen, J. L.; Bijen, J. M. J. M. *J. Mol. Struct.* **1973**, *16*, 289−297. (f) Moon, H.; Goldstein, J. H.; Simmons, J. W. *Spectrochim. Acta* **1960**, *16*, 1267. (g) Bouchy, A.; Demaison, J.; Roussy, G.; Barriol, J. *J. Mol. Struct.* **1973**, *18*, 211−217.

(11) (a) Verma, U. P.; Moller, K.; Vogt, J.; Winnewisser, M.; Christiansen, J. J. *Can. J. Phys.* **1985**, *63*, 1173−1183. (b) Scharpen, L. H.; Wollrab, J. E.; Ames, D. P.; Merritt, J. A. *J. Chem. Phys.* **1969**, *50*, 2063−2069. (c) Hencher, J. L.; Bauer, S. H. *J. Am. Chem. Soc.* **1967**, *89*, 5527−5531.

(12) (a) Stigliani, W. M.; Laurie, V. W.; Li, J. C. *J. Chem. Phys.* **1975**, *62*, 1890−1892. (b) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J.; Pratt, W. E.; Harmony, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 7837−7840. (c) Ramaprasad, K. R.; Laurie, V. W.; Craig, N. C. *J. Chem. Phys.* **1976**, *64*, 4832−4835. (d) Staley, S. W.; Norden, T. D.; Su, C.-F.; Rall, M.; Harmony, M. D. *J. Am. Chem. Soc.* **1987**, *109*, 2880−2884. (e) This numbering scheme differs from that used in Table 3. (f) Cheer, C. J.; Bernstein, D.; Greenberg, A.; Lyu, P.-C. *J. Am. Chem. Soc.* **1988**, *110*, 226−230.

(13) (a) Cox, A. P.; Thomas, L. F.; Sheridan, J. *Nature* **1958**, *181*, 1000−1001. (b) Sheridan, J. *Proc. Intern. Meeting Mol. Spectry. 4th, 1959* **1962**, *1*, 139−147; *Chem. Abstr.* **1963**, *59*, 8279e. (c) Costain, C. C.; Yarwood, J. *J. Chem. Phys.* **1966**, *45*, 1961−1965.

Table 1. Energies (hartrees) and Zero Point Vibrational Energies (ZPVE) for Cumulenes, Alkenes, Diazirines, and Cyclopropenes, SE (kcal/mol) for Isodesmic Reactions, and ΔE_{is} (kcal/mol) for Isomerization Reactions

R	−E(RCH=C=O)[a]	ZPVE[a]	−E(RCH=CH$_2$)[a]	ZPVE[a]	SE[a,b]	−E(RCH=N$^+$=N$^-$)[c]	ZPVE[c]	SE[c,d]	−E[RCH(N$_2$)][c]	ZPVE[c]	ΔE_{is}[c,e]	−E(RCH=C=CH$_2$)[c]	ZPVE[c]	SE[c,f]	−E[RCH(CH)$_2$][c]	ZPVE[c]	ΔE_{is}[c,g]	SE[c,h]	SE[c,i]	SE[c,j]
H	152.1601	0.0321	78.2943	0.0495	3.9	147.8438	0.0309	2.2	147.8361	0.0330	6.1	115.8611	0.0535	1.1	115.8230	0.0545	24.5	−0.4	−2.3	−2.7
Li	159.0446	0.0215	85.1356	0.0390	30.1	154.7018	0.0219	18.9	154.6674	0.0217	21.5	122.7219	0.0434	20.2	122.6328	0.0427	55.5	−6.2	10.9	5.0
BeH	166.8491	0.0297	92.9572	0.0477	19.6	162.4905	0.0300	16.7	162.4581	0.0301	20.4	130.4981	0.0515	7.3	130.4388	0.0514	37.1	−4.1	1.4	−2.6
BH_2	177.5170	0.0434	103.6262	0.0610	18.7	173.1285	0.0431	18.2	173.0931	0.0428	22.0	141.1244	0.0644	4.5	141.0751	0.0644	30.9	−2.6	0.8	−1.9
CH_3	191.3301	0.0593	117.4697	0.0775	0.0	186.8805	0.0589	0.0	186.8775	0.0600	2.6	154.8994	0.0813	0.0	154.8607	0.0815	24.4	0.0	0.0	0.0
NH_2	207.3367	0.0484	133.4913	0.0668	−9.3	202.8637	0.0489	−4.6	202.8659	0.0500	−0.7	170.8838	0.0714	−3.9	170.8483	0.0715	22.4	0.8	0.5	1.3
OH	227.1689	0.0357	153.3322	0.0545	−14.5	222.6820	0.0364	−9.6	222.6937	0.0378	−6.4	190.7089	0.0595	−5.0	190.6799	0.0594	18.1	4.8	−1.8	2.9
F	251.1482	0.0240	177.3152	0.0427	−16.9	246.6716	0.0244	−11.9	246.6913	0.0264	−11.2	214.7004	0.0474	−6.0	214.6834	0.0478	10.9	8.1	−5.6	2.5
Na	313.4382	0.0204	239.5226	0.0381	34.3	309.0862	0.0210	19.0	309.0532	0.0209	20.6	277.1038	0.0422	19.0	277.0179	0.0420	53.8		11.4	
MgH	351.7932	0.0264	277.8954	0.0442	23.2	347.4304	0.0267	14.9	347.3974	0.0267	20.7	315.4411	0.0482	10.3	315.3736	0.0480	42.3		4.3	
AlH_2	394.7214	0.0354	320.8285	0.0532	20.1	390.3414	0.0355	15.1	390.3062	0.0353	22.0	358.3461	0.0569	6.8	358.2879	0.0567	36.4		0.9	
SiH_3	442.3419	0.0472	368.4631	0.0653	11.5	437.9337	0.0470	7.5	437.9110	0.0473	14.4	405.9466	0.0689	4.1	405.8976	0.0688	30.6	−3.0	−2.1	−5.1
PH_2	493.5718	0.0403	419.7011	0.0583	6.3	489.1448	0.0406	6.0	489.1279	0.0411	10.9	457.1566	0.0625	1.8	457.1165	0.0626	25.3	−1.3	−3.4	−4.6
SH	545.7969	0.0319	475.9359	0.0498	0.2	545.3535	0.0321	1.5	545.3420	0.0326	7.5	513.3682	0.0541	−0.9	513.3344	0.0543	21.3	0.8	−5.6	−5.0
Cl	611.1843	0.0232	537.3361	0.0414	−7.7	606.7326	0.0233	−6.2	606.7357	0.0247	−1.0	574.7573	0.0459	−2.7	574.7338	0.0462	14.9	6.0	−9.3	−3.4
CF_3	(487.3439)[c]	0.0380[c]	(413.6568)[c]	0.0563[c]	−0.1[c]	483.4642	0.0377	−0.6	483.4564	0.0390	5.8	451.4834	0.0602	−0.5	451.4534	0.0607	19.1		−8.5	
CH=CH_2	(228.6070)[c]	0.0643[c]	(154.9197)[c]	0.0824[c]	−0.1[c]	224.7308	0.0642	1.4	224.7218	0.0653	6.3	192.7471	0.0866	−0.2	192.7067	0.0867	25.4		−1.1	
CH=O	265.1973	0.0419[c]	191.3286	0.0599[c]	5.4	260.5829	0.0420	7.2	260.5629	0.0425	12.9	228.5920	0.0637	1.3	228.5549	0.0641	23.3		−5.5	
C≡CH	228.0858	0.0414[c]	154.2249	0.0596[c]	0.5	223.5187	0.0413	1.3	223.5074	0.0425	7.8	191.5339	0.0637	−1.0	191.4970	0.0640	23.3		−4.0	
CN	244.1772	0.0314[c]	170.3161	0.0495[c]	0.6	239.5778	0.0312	0.7	239.5626	0.0322	10.1	207.5942	0.0536	0.9	207.5609	0.0539	21.1		−9.3	
NO	(280.3647)[c]	0.0300[c]	(206.6774)[c]	0.0481[c]	−0.1[c]	276.4932	0.0298	4.5	276.4778	0.0307	10.3	244.5027	0.0521	−1.4	244.4738	0.0526	18.4		−7.8	
NO_2	356.1684	0.0361[c]	282.3113	0.0542[c]	−1.9	351.3131	0.0357	0.3	351.3034	0.0370	6.9	319.3278	0.0582	−2.4	319.3078	0.0588	12.9		−13.1	
c-Pr	(267.6250)[c]	0.0926[c]	(193.9402)[c]	0.1108[c]	−1.6[c]															
Ph	(381.2742)[c]	0.1105[c]	(307.5854)[c]	0.1287[c]	0.9[c]															
NC												207.5602	0.0531	−3.8						
CH=C=CH_2												230.5740	0.0908							
CH=C=O												266.4322	0.0685							
N=C=O												282.4598	0.0583							
CH=N=N												262.5557	0.0684							
N_3												278.5397	0.0583							

[a] MP2/6-31G*//MP2/6-31G*. [b] ΔE for eq 1, including ZPVE. [c] HF/6-31G*//HF/6-31G*. [d] ΔE for eq 2, including ZPVE. [e] ΔE_{is} for eq 3, including ZPVE. [f] ΔE for eq 4, including ZPVE. [g] ΔE_{is} for eq 5, including ZPVE. [h] ΔE for eq 13. [i] ΔE for eq 14, including ZPVE. [j] ΔE for eq 15.

Table 2. Comparison of Experimental and Calculated (parentheses HF6-31G*; brackets MP2/6-31G*) Bond Distances (Å) and Bond Angles (deg) of Ketenes $H_nMC_2H_1{=}C_1{=}O_1$ and Allenes

Ketenes

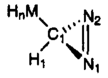
M	MC_2	C_2C_1	C_1O_1	MC_2C_1	$C_2C_1O_1$	ref
H	1.080(1.071)[1.080]	1.316(1.306)[1.318]	1.161(1.145)[1.180]	119.0(119.3)[119.6]	180.0(180.0)[180.0]	9a
H	1.090	1.315	1.163	118.3	180.0	9b
Me	1.518(1.512)[1.507]	1.306(1.305)[1.319]	1.171(1.149)[1.183]	122.6(123.3)[122.6]	180.5(180.0)[180.4]	9c
F	1.360(1.339)[1.366]	1.317(1.308)[1.325]	1.167(1.147)[1.183]	119.5(120.1)[119.7]	178.0(177.9)[178.2]	9d
Cl	1.726(1.731)[1.730]	1.316(1.308)[1.322]	1.161(1.142)[1.180]	119.8(120.8)[120.7]	180.0(179.2)[179.5]	9e
CN	1.427(1.424)	1.317(1.321)	1.167(1.133)	120.4(120.6)	(178.7)	9f

Allenes

M	MC_2	C_2C_1	C_1C_3	MC_2C_1	$C_2C_1C_3$	
H	1.087(1.076)	1.308(1.296)	1.308(1.296)	120.9(121.2)	180.0(180.0)	10a
Me	1.515(1.508)	1.301(1.297)	1.313(1.297)	124.0(121.3)	179.5(180.1)	10b
F	1.360(1.334)	1.301(1.292)	1.309(1.295)	121.9(121.3)	178.2(178.4)	10c
OMe(OH)	1.375(1.357)	1.318(1.297)	1.318(1.298)	125.3(121.6)	180.0(179.6)	10d
SMe(SH)	1.745(1.778)	1.327(1.293)	1.282(1.296)	125.4(121.3)	180.0(180.2)	10e
Cl	1.736(1.742)	1.309(1.292)	1.309(1.294)	122.2(121.1)	180.0(179.2)	10f
CN	1.409(1.440)	1.308(1.303)	1.308(1.290)	122.5(121.9)	180.0(179.5)	10g

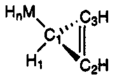
Table 3: Comparison of Experimental and Calculated (parentheses) Bond Distances (Å) and Bond Angles (deg)

diazirines:



M	MC_1	C_1N_1	N_1N_2	MC_1H_1	$N_1C_2N_2$	ref
H	1.080(1.074)	1.481(1.446)	1.228(1.194)	120.5(118.0)	49.0(48.8)	11a
CH_3	1.501(1.505)	1.481(1.444)	1.235(1.198)	122.3(120.5)[e]	49.3(49.0)	11b
F[a]	1.315(1.335)	1.426(1.403)	1.293(1.214)	111.8(112.5)	54.0(51.3)	11c

cyclopropenes:



M	MC_1	C_1C_2	C_2C_3	MC_1H_1	$C_3C_1C_2$	ref
H	1.088(1.083)	1.509(1.495)	1.296(1.276)	114.6(112.9)	50.8(50.5)	12a
CH_3[b]	1.521(1.520)	1.520(1.495)	1.294(1.278)	114.1(112.5)	50.4(50.6)	12b
F[c]	1.365(1.372)	1.438(1.457)	1.321(1.288)	105.6(108.1)	54.6(52.5)	12c
CN	1.453(1.465)	1.511(1.496)	1.292(1.272)	114.2(112.0)		12d
NO_2[d]	1.523(1.491)	1.483(1.469)	1.300(1.275)			12e

diazomethanes: $H_nMC_1H_1{=}N_1^+{=}N_2^-$

M	MC_1	C_1N_1	N_1N_2	$M_1C_1N_1$	$C_1N_1N_2$	ref
H	1.075(1.068)	1.300(1.280)	1.139(1.116)	117.0(117.9)	180.0(180.0)	13a,b
CN	1.424(1.417)	1.280(1.302)	1.132(1.103)	119.5(118.8)	180.0(179.2)	13c

[a] Difluorodiazirine. [b] 3,3-Dimethylcyclopropene. [c] 3,3-Difluorocyclopropene. [d] 1,2-Diphenyl-3-nitrocyclopropene. [e] $CH_3C_1N_1$.

ing frequencies.[5g] Slightly different values have been used,[3b,8d] but the differences do not change the conclusions.

To test the reliability of the calculated geometries these are compared to the available experimental data[9−13] from microwave measurements in Table 2 for ketenes and allenes and in Table 3 for diazirines, cyclopropenes, and diazomethanes. We have reported[5g] the calculation of infrared stretching frequencies for ketenes, and analogous values for diazomethanes and allenes are given in Table 4. Complete tables of all the geometries calculated are given in Tables A1−A21 and Figures A1−A15 (Supplementary Material).

Comparison of the experimental geometrical parameters for ketenes to those calculated at the HF/6-31G* and MP2/6-31G* levels reveal average deviations of the bond distances of 0.012 and 0.011 Å, respectively, and 0.5° and 0.4°, respectively, for the bond angles. In almost every case the HF/6-31G* calculated bond distances are less than the experimental values, while the MP2/6-31G* calculated values are larger than the experimental values, so if the calculated values were averaged the deviations would essentially vanish. Because of the systematic nature of the deviations and the ability of the HF/6-31G* calculations to reproduce the experimental values almost as well as do the MP2/6-31G* calculations, the former appear satisfactory for predictive and interpretive purposes.

For the diazomethanes and allenes, studied at the HF/6-31G* level, the average deviations between the experimental and calculated bond distances and bond angles are 0.02 Å and 0.05°, respectively. For the cyclopropenes and diazirines, the deviations in the bond lengths to the external substituents average 0.01 Å, with the calculated bonds usually being longer, whereas the calculated ring bonds are almost always considerably shorter, by an average value of 0.03 Å.

The precision of the experimental microwave values is often cited as ±0.01 Å for bond distances and ±0.5° for bond angles. The theoretical calculations are usually within this range, which lends confidence in the reliability and utility of the calculations.

Table 4. Calculated Infrared Stretching Frequencies (ν) and Intensities (I) of Allenes $MCH{=}C{=}CH_2$ and Diazomethanes $MCHN_2$ with Experimental[16] Values in Parentheses

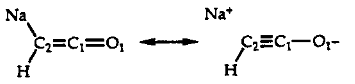
	allenes		diazomethanes	
M	ν (cm^{-1})^{a,b}	I (km/mol)^{a}	ν (cm^{-1})^{a,b}	I (km/mol)^{a}
H	1993 (1959)	80	2078 (2088)	777
Li	1823	388	2058	1490
BeH	1928	348	2155	965
BH_2	1938	383	2230	865
CH_3	2004 (1961)	50	2038 (2037–2074)	877
NH_2	2012	11	2040	808
OH^{a}	2018 (1955)^{c}	39	1987	635
F	2034 (1970)	21	1953	447
Na	1814	458	2026	1457
MgH	1901	319	2108	1248
AlH_2	1930	373	2170	1073
SiH_3	1966 (1932)^{d}	245	2115 (2070)^{d}	960
PH_2	1984	128	2110	995
SH	2003 (1938)^{e}	15	2094	878
Cl	2011 (1963)	6	2019 (2069)	748
CF_3	2016	93	2110	718
$HC{\equiv}C$	1994 (1975, 1950)	80	2076	1217
$HC{=}O$	1979 (1940–1960)	143	2201 (2110)^{f}	711
$N{=}O$	1987	99	2176	936
NO_2	2000	67	2168 (2105)	3528
CH_2CH	1989 (1950)	86	2053	1592
CN	1994 (1965, 1935)	98	2132	1093
CO_2H	1989 (1955)	173		

[a] HF/6-31G*//HF/6-31G*. [b] Scaled by 0.9. [c] CH_3O. [d] Me_3Si. [e] CH_3S. [f] t-BuCO.

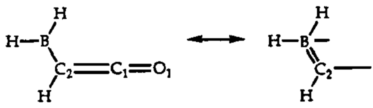
Atomic charges[7] calculated by the methods of Mulliken[7a] and the Natural Bond Orbital (NBO) method of Weinhold et al.,[7b] using the Gaussian package,[8a] and the zero-flux surface partitioning method of Bader[7c] using the AIMPAC package[7h] are listed in Tables 5–10 (supplementary material). The latter method is computationally very demanding and therefore the results are obtained only for the ketenes and alkenes, and not for all substituents.

Substituent Effects on Geometries. For the ketenes there is a systematic trend with longer C_1C_2 and shorter C_1O_1 bond lengths for electronegative substituents and the reverse for electropositive substituents. Thus at the HF/6-31G* level $FCH{=}C{=}O$ has C_1C_2 and C_1O_1 bond lengths of 1.308 and 1.147 Å, respectively, while $NaCH{=}C{=}O$ (**7**) has corresponding values of 1.282 and 1.171 Å. These trends are consistent with a contribution for the latter compound from the resonance structure **7a**, which involves donation by the C–Na bond. These trends are counteracted by the π-acceptor groups BH_2, $CH{=}O$, $N{=}O$, and NO_2 which have elongated C_1C_2 bonds, and shortened C_1O_1 bonds, consistent with the role of the resonance structure **8a**. Further evidence for the strong π-acceptor ability of the BH_2 group is the finding that the energy of the structure **8b**, which is constrained to a perpendicular geometry of the BH_2 group, is 18.9 kcal/mol less stable than **8a**.

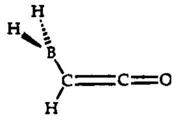
The same geometrical trends are observed at the MP2/6-31G* level, with the exception of sodioketene, which adopts a bridged geometry (**7b**), with the sodium almost equidistant from C_1, C_2, and O_1 and almost equivalent C_1C_2 and C_1O_1 bond lengths. This structure is 3.9 kcal/mol more stable than the alkynoate structure **7c** (HF/6-31G*//HF/6-31G*). For lithioketene a structure analogous to **7b** is not formed, presumably because the shorter lithium bond distances do not permit this type of bonding, and at the MP4/6-31G*//HF/6-31G* level the lithium ynolate structure analogous to **7c** is 4.4 kcal/mol less stable than the ketene structure.



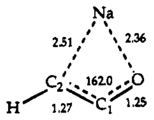
7 **7a**



8a



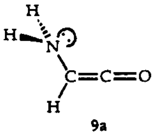
8b



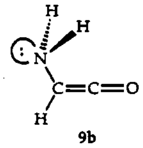
7b

7c

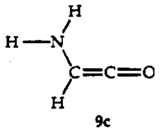
Substituents with lone pairs that can act as π-donors, especially NH_2, OH, PH_2, and SH, adopt twisted conformations in ketenes, as shown for NH_2 (**9a**) and OH (**10a**), in contrast to the situation in alkenes, where the substituents adopt coplanar geometries that permit π-donation, as in **9c** and **10b**. The most plausible explanation of this behavior is that π-donation by substituents is destabilizing in ketenes, as expected since there is a large coefficient of the HOMO at C_β (C_2), which would inhibit π-donation, and a low coefficient of the LUMO at this position. It has been suggested[14a] that the twisted geometry for $H_2NCH{=}C{=}O$ might arise from a stabilizing interaction between the lone pair on nitrogen and the in-plane electron-deficient p orbital at C_α, but our work indicates there is a negative Mayer bond order[14b] for this interaction, showing that no bonding occurs. The conformation **9b** is only 2 kcal/mol less stable than **9a** and 9.6 kcal/mol more stable than the planar conformation **9c** (MP2/6-31G*//MP2/6-31G*), also showing the absence of a major favorable bonding interaction between the nitrogen lone pair and C_α.



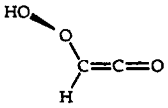
9a



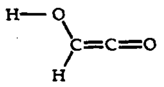
9b



9c



10a



10b

Structural effects in the diazomethanes are similar to those in the ketenes. There are no significant trends in the C_2N_1 and N_1N_2 bond lengths except for π-acceptor substituents, particularly $CH{=}O$, BH_2, NO, and NO_2, which show long C_1N_1 bonds and short N_1N_2 bonds, consistent with conjugation analogous to that shown in **8a** for ketenes. Just as for the BH_2-substituted ketene structure **8b**, the diazomethane structure with a BH_2 substituent fixed in a perpendicular geometry is much less stable, by 24.6 kcal/mol, than that with a planar BH_2 group, and the π-donor groups NH_2, OH, PH_2, and SH

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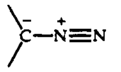
(14) (a) Footnote 12 in Brady, W. T.; Dad, M. M. *J. Org. Chem.* **1991**, *56*, 6118–6122. (b) Mayer, I. *Int. J. Quant. Chem.* **1986**, *29*, 477–483.

substituents on diazomethane also all adopt twisted conformations to minimize π-donation.

The calculated N_1N_2 bond lengths in substituted diazomethanes range from 1.095 Å for the BH_2 substituent to 1.134 Å for the fluoro substituent and are closer to that for molecular nitrogen (1.078 Å) than for typical compounds containing the N=N function such as the diazirines, which vary from 1.169 to 1.216 Å for the BH_2 and OH substituents, respectively, or HNNH (1.216 Å). Similarly the C_1N_1 bond lengths, which range from 1.256 to 1.333 Å for fluoro and BH_2 substituents, respectively, in the diazomethanes, are generally longer than those of N-substituted methylenimines $RN{=}CH_2$, which vary from 1.230 to 1.257 Å for the BH_2 and cyano substituents, respectively.[5f] Thus there is a large contribution to the diazomethane structure of the resonance form **11**, with C—N single bond and N—N triple bond character.



11

For diazirines and cyclopropenes the C_1N_1 and C_1C_2 bonds, respectively, are longest for the most electropositive substituent Li, and shortest for the most electronegative substituent F, while the N_1N_2 bond in diazirines and the C_2C_3 bond in cyclopropenes tend to show the opposite trend with electronegativity.

The variations in intraring bond lengths of diazirines and cyclopropenes as a function of substituent may be interpreted by the arguments which have been used to explain the comparable effects in cyclopropanes.[1g,2a] Thus for diazirines and cyclopropenes the molecular orbital with the highest coefficient on C_1 is antibonding at C_1N_1 for diazirines and C_1C_2 for cyclopropenes and bonding at N_1N_2 for diazirines and C_2C_3 for cyclopropenes. Electropositive substituents (σ donors) push electron density into this orbital, thereby lengthening C_1N_1 or C_1C_2, and shortening N_1N_2 or C_2C_3, while electronegative substituents cause the opposite effect.

π-Donation by the small rings to acceptor substituents explains why diazirine with the BH_2 substituent in the bisected conformation is 9.6 kcal/mol more stable than in the perpendicular conformation and cyclopropene substituted with BH_2 shows the same effect.[3e] This π-donation is via the ring HOMO, which is C_1N_1 bonding and N_1N_2 antibonding for diazirinyl and C_1C_2 bonding and C_1C_2 antibonding for cyclopropenyl. As expected for electron donation from this orbital the C_1N_1 and C_1C_2 bonds are longer and the N_1N_2 and C_2C_3 bonds shorter for the BH_2 derivatives than expected in the absence of this interaction.

The effects of π donor substituents on diazirines and cyclopropenes are expected to be strongest on the LUMO of the ring systems, which is bonding at C_1N_1 and C_1C_2 and antibonding at N_1N_2, or C_2C_3. Thus, π donors reinforce the σ-acceptor effect, making the C_1N_1 or C_1C_2 bonds even shorter and the N_1N_2 or C_2C_3 bonds even longer. Thus fluorodiazirine has the shortest C_1N_1 bond and the longest N_1N_2 bond. These effects are analogous to those in cyclopropanes.[1g,2a]

The calculated structural effects of substituents on allene geometries are rather small compared to those on ketenes and diazomethanes and resemble the trends found in alkenes. Thus electronegative substituents shorten both C_1C_2 and C_1C_3 bond lengths, which are 1.292 and 1.295 Å, respectively, for fluoroallene, compared to values near 1.303 and 1.300 Å for BeH. There is a strong preference of 8.8 kcal/mol for the BH_2 group to be coplanar with the adjacent allene function in BH_2-$CH{=}C{=}CH_2$ as opposed to the perpendicular geometry, just as for the alkene. The π-acceptor substituents CH=O, $CH{=}CH_2$, CH=C=O, and N=O all prefer coplanar *s-E* conformations. The π donor groups OH, NH_2, SH, and PH_2 prefer coplanar conformations, and in this respect the allenes resemble alkenes and not diazomethanes or ketenes.

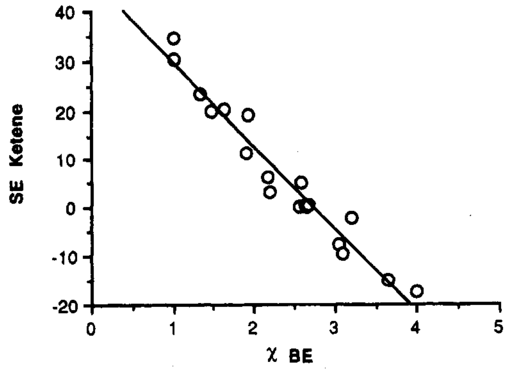
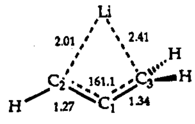
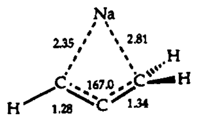


Figure 1. Correlation of MP2/6-31G* substituent stabilization energy (SE) of ketenes (eq 1) versus group electronegativity χ_{BE}.

Exceptional behavior is found for lithio- and sodioallene (**12, 13**), both of which prefer bridged structures even at the HF/6-31G* level. These structures resemble that found for sodioketene (**7b**) at the MP2/6-31G* level. The same structure for **12** has been found by computational studies[3b] and by experimental studies of derivatives of **12** in the solid state.[3b] The bending of the allenyl moiety in **12** has been attributed[3b] to the stabilizing interaction of the anionic lone pair orbital at C2 with the *anti*bonding π* orbital of the C1—C3 bond.



12



13

Energetics. In the current study we have extended the study of ketenes to include the effects of electron correlation using the MP2/6-31G*//MP2/6-31G* level of theory and the effects of zero point vibrational energy (ZPVE). However neither change causes a significant improvement in the quality of the correlations, as shown in equations 6–8 (Figure 1 for eq 8). This is not unexpected, since the energetic changes due to ZPVE energy are small and are expected to cancel in an isodesmic correlation,[8b] and while the energetic effects of electron correlation are significant these are also expected to cancel in an isodesmic comparison.[8b] These results indicate that the energies obtained at the HF/6-31G*//HF/6-31G* level for diazomethanes, allenes, and other substrates will give close correspondence with values obtained at higher levels.

$$SE(\mathrm{HF}) = -15.6\chi_{BE} + 42.3 \quad (r = 0.98) \quad (6)$$

$$SE(\mathrm{HF_{ZPVE}}) = -15.1\chi_{BE} + 41.3 \quad (r = 0.98) \quad (7)$$

$$SE(\mathrm{MP2}) = -17.0\chi_{BE} = 46.4 \quad (r = 0.97) \quad (8)$$

As discussed above, there is a strong geometric preference for the π-acceptor substituents BH_2, CH=O, NO, and NO_2 to adopt coplanar geometries, and the deviations of these substituents above the correlation lines may be attributed to the stabilization due to conjugation; for ketenes this amounts to 5.3, 3.0, 5.8, and 6.1 kcal/mol, respectively, at the MP2/6-31G* level, except for NO, which is at the HF/6-31G* level.

Ketenes are destabilized by π-donor groups and for the NH_2, OH, and SH substituents the twisted geometries (**9a** and **10a** for the former two substituents) shown are stabilized relative to coplanar structures by 11.6, 4.0, and 6.8 kcal/mol; no structure for a coplanar PH_2 group could be calculated.

The cyclopropyl group is 4.1 kcal/mol more destabilizing toward a ketene than predicted by eq 1. This effect would be predicted both by the π-donor ability of cyclopropyl and by the enhanced σ-acceptor character of this group due to rehybridization at carbon,[1g,2a,15a–e] which does not appear to be reflected in the group electronegativity of cyclopropyl (2.57), which is almost identical to that of CH_3 (2.55).[6]

A number of conjugating substituents including $CH{=}CH_2$, $C{\equiv}CH$, Ph, and CN give SE values that are in the range ±2 kcal/mol both for ketenes and diazomethanes. These substituents all have the ability to act as both π donors and π acceptors, including CN,[15f] and are bonded to the ketenyl moiety with sp or sp^2 atoms that would have enhanced electronegativities. Any energetic effects due to these causes appear to cancel or to be offset by other effects, so that the net effects are almost zero.

The effect of substituents on diazomethanes, as defined by the isodesmic energy reaction of eq 2, is similar to that for ketenes, although the total range of the SE values of 30.9 kcal/mol is significantly less than that for ketenes of 45.8 kcal/mol at the HF/6-31G* level, and the correlation of SE values with group electronegativities χ_{BE} (eq 9) gives a lower correlation coefficient of 0.93 compared to 0.98 for the ketenes (Figure 2). This scatter for the diazomethanes arises largely from the large positive deviations from the correlation by the π-acceptor substituents BH_2, $CH{=}O$, $N{=}O$, and NO_2 of 8.4, 4.6, 7.4, and 4.2 kcal/mol, respectively. On average these deviations are significantly larger than those for the corresponding ketenes, while the total range of the effects is smaller. The large stabilization by π-acceptor groups is consistent with the well-known stabilization of α-acyldiazo compounds as represented in structure **14c**, and this conjugative stabilization appears to be relatively more important for diazomethanes than for ketenes.

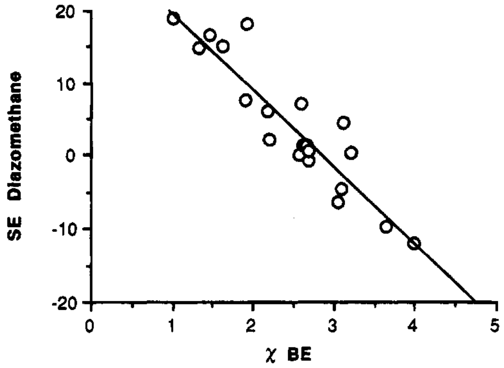


Figure 2. Correlation of HF/6-31G* + ZPVE substituent stabilization energy (SE) of diazomethanes (eq 2) versus group electronegativity χ_{BE}.

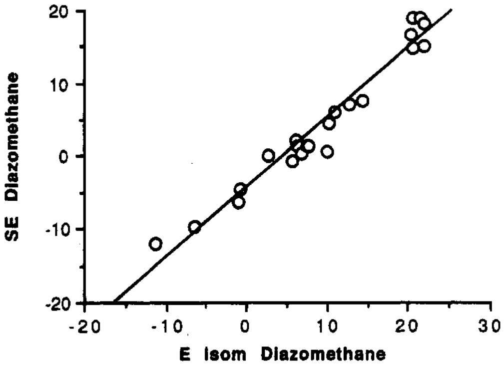
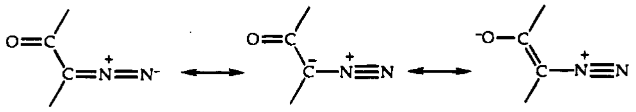


Figure 3. Correlation of HF/6-31G* + ZPVE substituent stabilization energy (SE) of diazomethanes (eq 2) versus ΔE_{is} of diazomethanes into diazirines (eq 3).

$$SE = -10.6\chi_{BE} + 30.2 \qquad (9)$$



14a **14b** **14c**

The calculated isomerization energy of diazomethanes to diazirines, namely the energy change for eq 3 based on the calculated energies of the two species involved, is particularly revealing. These values range from 22.0 kcal/mol for the highly electropositive substituents BH_2 and AlH_2 to −11.2 kcal/mol for the F substituent. There is a linear correlation between ΔE_{is} and group electronegativity (eq 10) with a fair correlation coefficient $r = 0.90$ and a rather good correlation (Figure 3) between the SE values of diazomethanes and ΔE_{is}, $r = 0.98$ (eq 11).

$$\Delta E_{is} = -10.5\chi_{BE} + 34.8 \qquad (10)$$

$$SE = 0.95\Delta E_{is} - 4.5 \qquad (11)$$

Thus the major influence on the diazomethane/diazirine isomerization is the substituent effect on the stability of the diazomethane. This agrees with experience, in that diazomethane substituted with the electropositive group Me_3Si is quite stable, in agreement with the calculation, whereas difluorodiazomethane is unknown and is calculated to be unstable,[4c,5c] while difluorodiazirine is quite stable.[11c]

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(15) (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) Halton, B.; Banwell, M. G. In *The Chemistry of the Cyclopropyl Group*, Rappoport, Z., Ed.; Wiley: London, 1987. (d) Billups, W. E.; Bachman, W. E. *Tetrahedron Lett.* **1992**, *33*, 1825–1826. (e) Walsh, R.; Untiedt, S.; de Meijere, A. *Chem. Ber.* **1994**, *127*, 237–245. (f) Dixon, D. A.; Eades, R. A.; Frey, R.; Gassman, P. G.; Hendewerk, M. L.; Paddon-Row, M. N.; Houk K. N. *J. Am. Chem. Soc.* **1984**, *106*, 3885–3891. (g) Lias, S.G.; Bartmess, J. E.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1, 111. (h) This calculation was carried out using the facilities of the San Diego Supercomputer Center.

(16) (a) Runge, W. In *The Chemistry of the Allenes*; Landor, S. R., Ed., Academic Press: New York, 1982; Vol. 3, Chapter 10. (b) Runge, W. *Prog. Phys. Org. Chem.* **1981**, *13*, 315–484. (c) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G; Grasselli, J.G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: London, 1991. (d) Regitz, M.; Maas, G. *Diazo Compounds*, Chapter 1; Academic Press, Inc.: New York, 1986. (e) Bohshar, M.; Fink, J.; Heydt, H.; Wagner, O.; Regitz, M. In *Methoden der Organischen Chemie*, Vol. E14b, Part 2; Georg Thieme Verlag: Stuttgart, 1990; pp 961–1371.

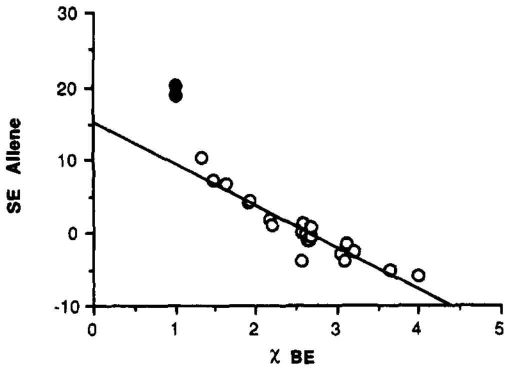

Figure 4. Correlation of HF/6-31G* + ZPVE substituent stabilization energy (SE) of allenes (eq 4) versus group electronegativity χ_{BE} (omitting dark points)

The stabilization energies of the allenes (eq 4) range from 20.2 and 19.0 kcal/mol for the Li and Na derivatives to −6.0 kcal/mol for the fluoro substituent. It is striking that the SE values for Li and Na are much larger than for any other substituents, and a plot of SE versus χ_{BE} shows a large deviation for the Li and Na derivatives. However if the points are omitted a fairly good correlation SE = $-5.8\ \chi_{BE} + 15.3$, $r = 0.94$, is found (Figure 4). As noted above lithio- and sodioallene have bridged structures (**12**, **13**), and if the deviations of these substituents from the linear correlation are attributed to the extra stabilization resulting from this interaction, these total 11 and 9 kcal/mol for lithium and sodium, respectively.

The remaining effect of substituents on allene stabilities covers a total range of 16.3 kcal/mol, which is much smaller than for ketenes or diazomethanes. There do not appear to be any significant deviations for π-acceptor substituents, and the π-donor groups NH_2, OH, PH_2, and SH adopt coplanar geometries just as for alkenes. There is a significantly greater substituent effect on allenes compared to alkenes, and this may be attributed to the strongly electronegative sp-hybridized carbon found in the former.

In a previous study[3a] of substituent effects on allenes obtained from molecular orbital calculations, the isodesmic stabilization energies for a smaller group of substituents were correlated with the field and resonance parameters F and R. However the data set was not large enough for a definitive test of a dual parameter equation, and the current test shows that this is unnecessary.

Values of E_{is} for conversion of allenes to cyclopropenes (eq 5) range from 10.9 kcal/mol for the fluoro substituent to 55.5 kcal/mol for Li, and there is a good correlation (Figure 5) SE = $0.56\ \Delta E_{is} - 12.7$, $r = 0.97$. The greater stability of the allenes in every case may be attributed to the strain present in the cyclopropenes, and the absence of large destabilizing effects due to electronegativity in the allenes. The thermal isomerization of substituted cyclopropenes to allenes is a known process.[15d,e] The large range in E_{is} is indicative that there are major substituent effects operative in the cyclopropenes. Experimentally the difference in ΔH_f for allene and cyclopropene is (20.4 ± 0.9) kcal/mol,[15g] and for HF/6-31G* optimized geometries the calculated energy difference is 24.5, 18.9, 21.0, and 21.9 kcal/mol at the HF/6-31G*, MP2/6-31G*, MP3/6-31G*, and MP4/6-31G* levels, respectively.[15h] Thus the MP2 and higher levels of theory give satisfactory agreement with the experimental differences.

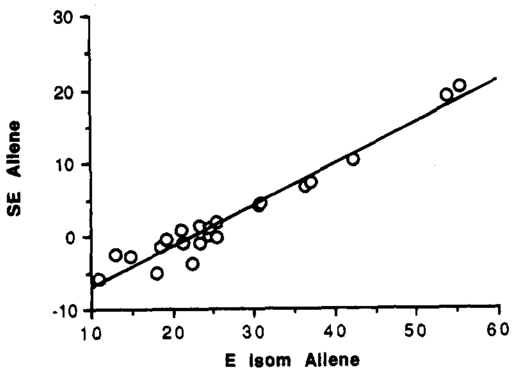

Figure 5. Correlation of HF/6-31G* + ZPVE SE of allenes (eq 4) versus ΔE_{is} of allenes into cyclopropenes (eq 5).

There have been previous theoretical studies of substituent effects in cyclopropenes,[3d,e] but even the most comprehensive of these[3e] included only the second period substituents, plus CN and NC, and utilized HF/6−31G* single point energy calculations on HF/3-21G-optimized geometries. We have now examined a larger group of substituents, including the third period, with HF/6-31G*-optimized geometries. Also we can utilize recently published[2a] data on substituted cyclopropanes to interpret the effect on cyclopropenes. Thus for the isodesmic exchange between isopropyl and cyclopropyl derivatives (eq 12), there was found a linear correlation with substituent electronegativity over a 13.9 kcal/mol energy span, with cyclopropyl substitution favored for electropositive substituents.[2a] This was ascribed[2a] to the strong electronegativity of the cyclopropyl group, arising from the high s character of the exocyclic orbitals. The major deviation is for BH_2, which is even more stabilizing as a cyclopropyl substituent, and this is attributed to conjugative electron donation from the cyclopropyl to BH_2.[2a]

$$c\text{-PrX} + i\text{-PrH} \rightarrow c\text{-PrH} + i\text{-PrX} \qquad (12)$$

Substituent effects on cyclopropenes compared to cyclopropanes[2a] by the isodesmic reaction of eq 13 are given in Table 1 and cover a range in isodesmic energies from −6.2 kcal/mol for lithium to 8.1 kcal/mol for Cl for a total span of 14.3 kcal/mol, with substitution on cyclopropenyl favored by electronegative groups,[12f] and disfavored by electropositive substituents. This trend may be explained as a manifestation of incipient antiaromatic character in the cyclopropenes substituted with electropositive groups and aromatic stabilization of cyclopropenes with electronegative substituents. Thus as shown for lithiocyclopropene (**15**) and fluorocyclopropene (**16**) the extreme resonance structures **15a** and **16a** involve 4π antiaromatic and 2π aromatic structures, respectively. An earlier study[3d] of cyclopropenes detected a "hint" of antiaromaticity in **15**, and the molecular structures of 3-cyanocyclopropene[12d,e] and 3-nitro-1,2-diphenylcyclopropene[12e,f] were also interpreted in terms of incipient stabilization as in **16a**. Antiaromatic destabilization of the planar cyclopropenyl anion causes this species to adopt a structure with C_s symmetry, with two hydrogens below and one above the ring plane.[17]

Substituent effects on diazirines relative to cyclopropenes and cyclopropanes[2a] are evaluated according to eqs 14 and 15, respectively, as compiled in Table 1. There

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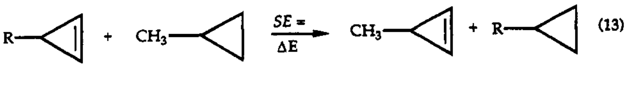
[17] (a) Li, W.-K. *J. Chem. Res. S* **1988**, 220–221. (b) Hess, B. A., Jr.; Schaad, L. J.; Carsky, P. *Tetrahedron Lett.* **1984**, *25*, 4721–4724. (c) Winkelhofer, G.; Janoschek, R.; Frater, F.; Spitznagel, G. W.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 332–337.

Table 11. Correlation of Charges with Group Electronegativities χ_{BE}

	Mulliken		NBO		Bader	
substrates	slope	*r*	slope	*r*	slope	*r*
ketenes	0.24	0.87	0.43	0.96	0.63	0.88
alkenes	0.21	0.85	0.42	0.95	0.47	0.86
diazomethanes	0.24	0.88	0.46	0.96		
diazirines	0.23	0.90	0.44	0.97		
alkenes	0.20	0.80	0.38	0.92		
cyclopropenes	0.21	0.88	0.43	0.97		
isocyanates[a]	0.14	0.75	0.33	0.96		
imines[a]	0.19	0.82	0.39	0.96		

[a] References 5f.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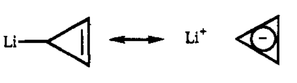
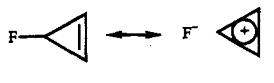
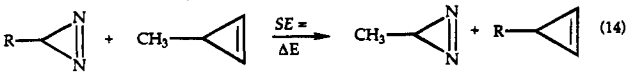

15 15a


16 16a

is a large span of 24.9 kcal/mol for eq 14, with diazirines highly favored by the strongly electropositive substiuents, especially Li and Na, and the cyclopropenes strongly favored by F and Cl. A strongly electronegative character of the diazirinyl group would seem to contribute to these effects, although the overall correlation of ΔE with substituent electronegative is only fair. There is a range of 10.1 kcal/mol in the SE values in the comparison of substituted diazirines and cyclopropanes (eq 15), with a notable trend being that the third-period groups all favor cyclopropyl substitution, by at least 5 kcal/mol, relative to corresponding second period groups.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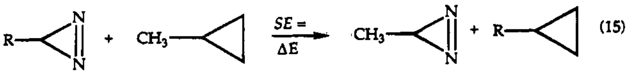

(15)

Atomic Charges. The evaluation of the atomic charges obtained by the different methods may be done in various ways. One is the correlation of the charge on the substituted atom with the substituent electronegativity, and the results of such correlations are compared in Table 11. These correlations for Mulliken charges have slopes of between 0.14 and 0.24, with correlation coefficients of 0.75 to 0.90, while the NBO-derived charges give slopes of 0.33 to 0.46 and correlation coefficients of 0.92 to 0.97. Thus the variation in the charges, as indicated by the slopes, is twice as large by the NBO method, with decidedly better correlations. The Bader charges give even greater variations in the charges, as indicated by the slopes of 0.47 and 0.63, but the correlation coefficients of 0.86 and 0.88 are similar to those found with the Mulliken charges.

Thus the trends in the charges obtained by all three methods are similar, although the largest and smallest variations in charge are obtained by the Bader and Mulliken methods, respectively. However the best correlation with substituent electronegativity is obtained with the NBO method, and because of the general utility and widespread applicability of these parameters the NBO method seems most attractive for obtaining meaningful atomic charges.

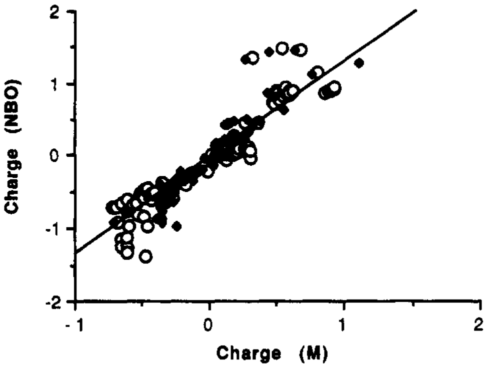


Figure 6. 6. Correlation of calculated Natural Bond Orbital (NBO) charges of ketenes (open circles) and alkenes (dark) with calculated Mulliken charges (M).

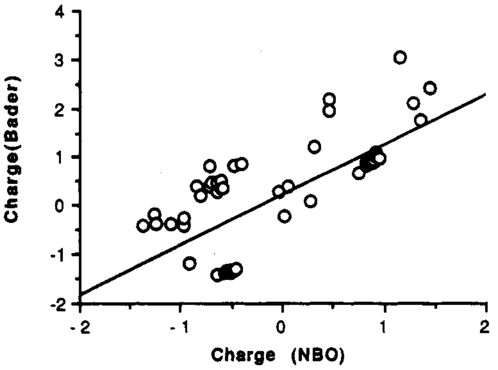


Figure 7. Correlation of calculated Bader atomic charges with Natural Bond Orbital (NBO) atomic charges for ketenes.

The charges obtained by the NBO method give the correlations of eq 16 and 17, for alkenes and ketenes, respectively, with the corresponding Mulliken changes, and an overlap plot of these correlations is given in Figure 6. Correlations of the NBO or Mulliken charges with Bader charges give the much poorer correlations of eqs 18 and 19, respectively, as shown in Figure 7 for eq 19.

$$\text{charge(NBO)} = 1.63(\text{charge Mulliken}) + 1.06 \times 10^{-3} \quad (r = 0.93) \quad (16)$$

$$\text{charge(NBO)} = 1.36(\text{charge Mulliken}) + 3.62 \times 10^{-3} \quad (r = 0.95) \quad (17)$$

$$\text{charge(Bader)} = 1.52(\text{charge NBO}) + 0.022 \quad (r = 0.69) \quad (18)$$

$$\text{charge(Bader)} = 1.02(\text{charge NBO}) + 0.211 \quad (r = 0.71) \quad (19)$$

From these results it may be concluded that charges calculated by the Mulliken and NBO methods give comparable results, although the range of charges calculated by the latter method is somewhat larger The largest deviations from the correlations are associated with the large positive NBO charges on Be, Mg, and Al (1.33, 1.44, and 1.45, respectively for alkenes, and 1.35, 1.48, and 1.45, respectively, for ketenes), and the large negative charges at the corresponding substituent bonded carbons of −1.11 to −1.38 at C_1 for ketenes and −0.86 to −0.97 at C_2 for alkenes. Thus the NBO method indicates a much greater ionic character for the C—metal bonds compared to the Mulliken method. Interestingly the Bader method indicates even greater positive charge on these metal atoms (1.75 to 3.03 for Be, B, Mg, Al, and Si for alkenes and ketenes). However the Bader method shows the negative charges in these compounds are distributed more to the metal and carbon-bonded hydrogen atoms, as compared to the NBO and Mulliken charges. The Bader charges on oxygen are all in a narrow range from −1.31 for the NO_2 substituent to −1.43 for Li, showing a large negative charge which is only moderately affected by the π-acceptor character of NO_2 and the donor character of Li.

Comparison of the NBO charges of the substituted carbons of the ketenes to those of the corresponding alkenes show that the negative charge at this carbon is greater by 0.33 to 0.43 electron for the various substituents, and this high negative charge at C_2 of ketenes is consistent with the known reactivity and ^{13}C NMR chemical shifts of these compounds.[18]

For diazomethanes a similar trend in the charges at the substituted carbon with that of alkenes is found, with the former being more negative by an almost constant 0.35 electron, while for allenes the substituted carbon is also more negative than for alkenes, but by an average of only 0.1 electron, showing that the allenes are considerably less polarized than are ketenes and diazomethanes.

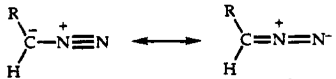
Thus while the relative charges obtained by the NBO method give the best correlation with substituent electronegativities, it has been suggested[7g] that while the Bader charges do have a well-defined physical significance, they are "completely unsuited in the framework of the nuclei-centered point-charge models of molecular properties," and they should not be used within oversimplified models. Thus comparison of the Bader charges for ketene to those of ethylene shows that the CH_2 carbon in the former is indicated to be positively charged, and by 0.32 electron more than the carbons in ethylene. However the interpretation of the high-field ^{13}C NMR shift of this carbon in ketene and the dipole moment both indicate this carbon has excess negative charge.[18]

The Bader charges show extreme values of charge, for example the CF_3 groups in $CF_3CH{=}C{=}O$ and CF_3-$CH{=}CH_2$ both have negative charges of −0.75 on each fluorine and a positive charge of 2.04 on carbon, indicating a strikingly high degree of ionic character to this group, while the SiH_3 groups in $SiH_3CH{=}C{=}O$ and SiH_3-$CH{=}CH_2$ have positive charges on silicon of 3.03 and 3.01, respectively, and the hydrogens each have a negative charge of −0.75. These high charges are indicative that charges calculated by the Bader method for these molecules give values that are different from conventional chemical expectations.

An independent comparison of atomic charges of acylketenes calculated by the Mulliken, NBO, and Bader (CHELPG) methods has appeared[7i] and is in harmony with that given here.

Infrared Spectra. We have presented[5g] a detailed comparison of the calculated and observed ketene band infrared frequencies. For allenes comparison of the calculated and observed IR[16a−c] frequencies for the C=C=C asymmetric stretch (Table 4) shows that the former are consistently less than the observed values, by an average of 48 cm^{-1}. The overall range of the observed frequencies is only 38 cm^{-1}, and for both the calculated and observed frequencies there is a decrease in the frequencies with decreasing electronegativity. This is consistent with the results for the ketenyl group,[5g] for which there is a linear dependence of the frequencies with the field or inductive substituent parameter F. There is also a reasonable correlation of calculated allene and ketene frequencies.

The effect of substituents on the frequencies of the diazomethyl group have been interpreted[16c] as being due to the inductive and resonance effects of the substituent, and in particular the ability to conjugatively stabilize the negative charge on carbon in **17a**, which has high N−N triple bond character and causes a shift to higher frequencies.



17a **17b**

As seen in Table 4 the calculated frequencies for the diazomethanes differ from the reported[16c−e] values by as much as 100 cm^{-1}, and furthermore there is no discernible trend in the deviations. It is also known[16d] that the measured values are medium dependent, but this is also true for ketenes and allenes, yet the calculated values for the latter two are of some diagnostic value. The reasons for the greater discrepancies between calculated and experimental diazomethane parameters are not apparent at present.

In summary the calculated structures and energies of ketenes, diazomethanes, diazirines, allenes, and cyclopropenes reported here are of great utility in the understanding of many properties of this species. In addition several methods for the calculation of atomic charges are compared and calculated IR frequencies of cumulenes are evaluated.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. We are grateful to Prof. R. F. W. Bader for providing a copy of the AIMPAC package (ref 7h) and to a referee for helpful comments.

Supplementary Material Available: Mulliken, NBO, and Bader charges, calculated bond lengths, bond and dihedral angles, and optimized structures of ketenes, alkenes, diazomethanes, diazirines, allenes, and cyclopropenes (42 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(18) Tidwell, T. T. *Ketenes*; John Wiley; New York, in press.