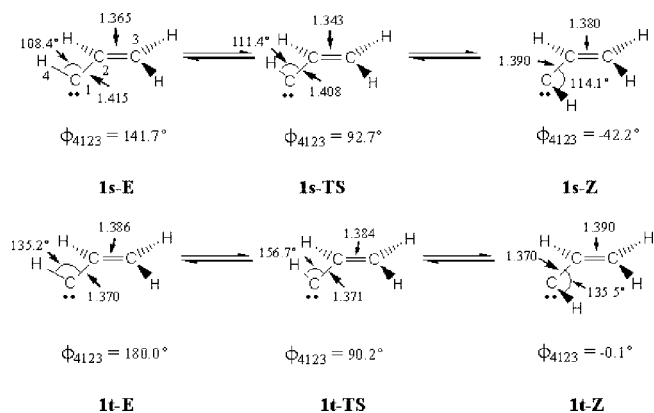




CHART 1



The molecular assemblage represented by vinylcarbene (**1**) is more complicated than its cationic, radical, and anionic relatives due to the fact that the nonbonding electron pair may be paired or unpaired providing a singlet or triplet species. Although difficulties in analyzing the resonance energies of allyl cation and anion by evaluating the rotational energy barrier have been discussed,<sup>2,2b-e</sup> it seemed reasonable to anticipate that a review of the rotational energy barriers for vinylcarbenes using density functional theory and G3 theory, without symmetry restrictions, would be a good starting point. Light might be shed on the resonance energies as well as on the intrinsic nature of these processes. As will be noted below, a symmetry restriction is imposed to achieve the orthogonality required for components of eq 2.

## Results and Discussion

The geometric changes upon rotation of the singlet from the s-E conformation (**1s-E**) over the transition state (**1s-TS**) to the s-Z conformation (**1s-Z**) and the related triplet values for **1t-E**  $\rightleftharpoons$  **1t-TS**  $\rightleftharpoons$  **1t-Z** were evaluated at the B3LYP/6-31G(d) level<sup>6a</sup> and are compared with the results of Yoshimine and co-workers<sup>5e,f</sup> (Chart 1). The energies were determined at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)<sup>7</sup> and G3//B3LYP levels<sup>8</sup> (Table 1).

(6) (a) The density functional theory calculations employed Becke's three-parameter hybrid method. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652, and the correlation functional of Lee, Yang, and Parr within Gaussian 03. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *785*–789. Within the Gaussian 03, Revision D.01: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W. C.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Wallingford, CT, 2004. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.

(7) (a) Freeman, P. K.; Dacres, J. E. *J. Org. Chem.* **2003**, *68*, 1386–1393. (b) Freeman, P. K.; Pugh, J. K. *J. Org. Chem.* **2000**, *65*, 6107–6111. (c) Freeman, P. K.; Pugh, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 2269–2273. (d) Freeman, P. K.; Pugh, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 2269–2273. (e) Freeman, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 161916–20. (f) See also: Bettinger, H. F.; Schleyer, P. v. R.; Schreiner, P. R.; Schaefer, H. F., III. In *Modern Electronic Structure Theory and Applications in Organic Chemistry*; Davidson, E. R., Ed.; World Scientific: New Jersey, 1997; Chapter 3.

TABLE 1. Rotational Barriers for Vinylcarbenes<sup>a</sup>

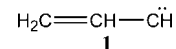
spin state	B3LYP/6-311+G(3df,2p)// B3LYP/6-31G(d) + ZPE at B3LYP/6-31G(d) <sup>b</sup>		G3//B3LYP	
	(1s-TS)-(1s-E)	(1s-TS)-(1s-Z)	(1s-TS)-(1s-E)	(1s-TS)-(1s-Z)
singlet	5.49, 8.4 <sup>c</sup>	5.46, 6.6 <sup>c</sup>	7.10	6.22
triplet	4.06, 4.6 <sup>c</sup> (5.7) <sup>d</sup>	3.39, 4.6 <sup>c</sup> (5.7) <sup>d</sup>	4.54	4.17

<sup>a</sup>  $N_{\text{imag}} = 0$  for ground states,  $N_{\text{imag}} = 1$  for the transition states.

<sup>b</sup> Singlets are restricted, triplets unrestricted; ZPE scaled at 0.96 to be consistent with the G3//B3LYP calculations, ref 8.

<sup>c</sup> Reference 5f SDQC1/DZP//HF/DZP *trans/cis* isomerization of planar carbenes.

<sup>d</sup> Reference 5e MRCI/DZP//MCSCF/4-31G.



In analyzing the geometric changes in Chart 1, the carbon–carbon bond distances of both the singlet and triplet species approach 1.38 Å, which is appropriate for a bond order of 1.5 and supports the presence of resonance stabilization. The rotational energy barrier for the singlet (**1s-TS**–**1s-E**) (5.49, 7.10 kcal/mol) is, indeed, greater than that for the triplet (**1t-TS**–**1t-E**) (4.06, 4.54 kcal/mol), which is reflected in the lengthening of the C-1–C-2 bond and the tightening up of the C-2–C-3 bond in **1s-TS** (vs **1t-TS**). In the singlet, overlap of the p-orbital at C-1 with the vinyl  $\pi$ -system will be broken, although for the originally in-plane carbene  $sp^2$  like orbital, some back-electron donation is possible. This would result in the barrier being less than the pure resonance energy in the ground state. The NPA charge<sup>6a</sup> changes for the singlet upon rotation, Table 2, **1s-TS**–**1s-E**, are consistent with shutting down of cationic p- $\pi$  resonance: C1 becomes more positive (0.179), C2 undergoes little change (0.061), while C3 becomes more negative (–0.340). One cannot rule out, however, some back bonding, since it would enhance the trend expected for the diminution of p- $\pi$  resonance. As has been noted in the case of the allyl ions, hyperconjugation may play a role in stabilization of the rotational transition state.<sup>2c,d</sup>

In the triplet there is little change in C1–C2 and C2–C3 bond lengths upon rotation. The wider angle, H4C1C2, in the rotational transition state suggests movement toward an sp-hybridized carbon. This leads to allylic radical delocalization for the original in plane orbital and is consistent with the lower energy barrier for rotation (4.06, 4.54 kcal/mol). The changes in charge for the triplet **1t-TS**–**1t-E** for C1, C2, and C3, –0.029, 0.022, and 0.007, respectively, (Table 2), provide a clear contrast with those for the singlet, exhibiting minimal charge separation. It is clear that the rotational barrier for the triplet does not shut down conjugation and so is not a good measure of conjugation and thus resonance.

A second approach for the analysis of vinylcarbenes involves calculations of the energy changes in the isodesmic equation (1), carried out at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) and G3//B3LYP levels, Table 3. The stabilization energy evaluated in this way, especially in the case of the singlet, involves both resonance and inductive effects.

The resonance and inductive effects are separated out using the approach developed by Barbour and Karty<sup>2b</sup> that involves, in this case, comparing the series ( $n = 1-3$ ) for eqs 2 and 3, which may be combined by subtracting 2 from 3 to yield

(8) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 77650–7657.

**TABLE 2.** NPA Charges at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) (Charges(s) on Hydrogens Summed into Carbons)

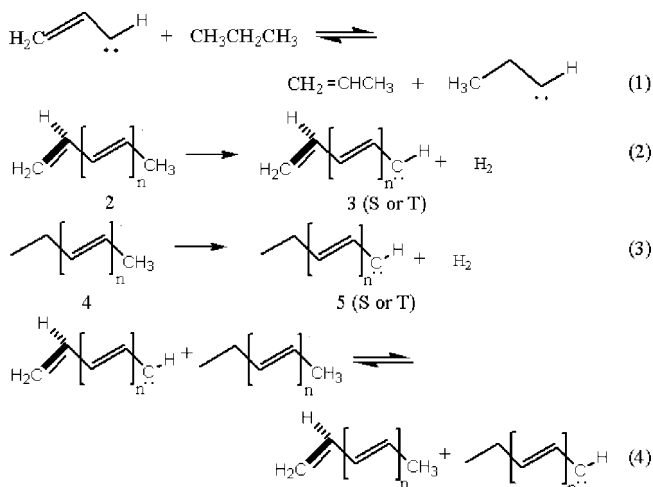
singlet	1s-E	1s-TS	1s-Z	$\Delta\text{ch}(1\text{s-TS}) - (1\text{s-E})^a$	$\Delta\text{ch}(1\text{s-TS}) - (1\text{s-Z})^a$
C(1)H	-0.010	0.169	0.007	0.179	0.162
C(2)H	-0.176	-0.115	-0.136	0.061	0.021
C(3)H <sub>2</sub>	0.286	-0.054	0.128	-0.340	-0.182
triplet	1t-E	1t-TS	1t-Z	$\Delta\text{ch}(1\text{t-TS}) - (1\text{t-E})^a$	$\Delta\text{ch}(1\text{t-TS}) - (1\text{t-Z})^a$
C(1)H	0.138	0.109	0.142	-0.029	-0.033
C(2)H	-0.195	-0.173	-0.190	0.022	0.017
C(3)H <sub>2</sub>	0.057	0.064	0.048	0.007	0.016

<sup>a</sup> Changes in charge, transition state–ground state, for the species denoted.

**TABLE 3.** Stabilization Energies of Vinylcarbenes from eq 1

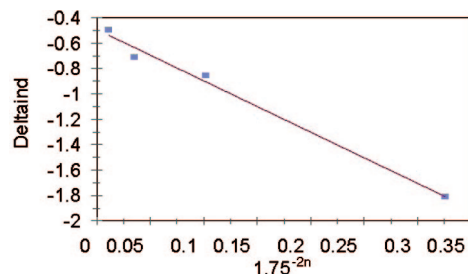
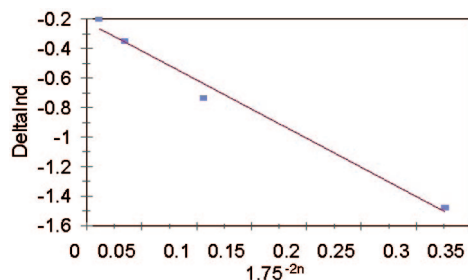
	B3LYP/6-311+G(3df,2p)// B3LYP/6-31G(d) + ZPE at B3LYP/6-31G(d) (kcal/mol)	G3//B3LYP (kcal/mol)
singlet	4.65	4.76
triplet	13.89	11.68

isodesmic equation (4). The geometry of the ultimate double bond in series 2 is fixed so that its p-orbitals are orthogonal with the remaining  $\pi$  system. Thus, the energy change in eq 2 can only involve the inductive effect of the ultimate vinyl group, and eq 4 should correspond to the inductive difference between vinyl and ethyl for each member of the series ( $\Delta_{\text{inductive}}$ ). Plotting  $\Delta_{\text{inductive}}$  versus  $1.75^{-2n}$ , using the through-bond inductive model of Bianchi et al.,<sup>9</sup> and extrapolation to  $n = 0$  yields the inductive difference between vinyl and ethyl in the parent series in eq 1, avoiding the features of back bonding, hyperconjugation, and carbene angle changes which cloud the picture with the rotational analyses.



The inductive difference extrapolation for equation 4 ( $n = 4 \rightarrow 0$ ) for the singlet states at the B3LYP/6-311+G(3df, 2p)//B3LYP/6-31G(d) + ZPE at B3LYP/6-31G(d) level provides a correlation ( $R = 0.995$ ) and a  $\Delta_{\text{inductive}}$  value at  $n = 0$  of  $-4.52$  (Figure 1). At the G3(MP2)//B3LYP level, an analogous plot of  $\Delta_{\text{inductive}}$  versus  $1.75^{-2n}$  exhibits an equally good correlation ( $R = 0.993$ ) and a value for  $\Delta_{\text{inductive}}$  of  $-4.16$  at  $n = 0$  (Figure 2). These values, in line with expectation, indicate

(9) Bianchi, G.; Howarth, O. W.; Samuel, C. J.; Vlahov, G. *J. Chem. Soc., Perkin Trans. 2* **1995**, 7, 1427–1432.

**FIGURE 1.** Plot of  $\Delta_{\text{inductive}}$  calculated at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) + ZPE at B3LYP/6-31G(d) versus an attenuation factor of  $1.75^{-2n}$  ( $n =$  number of double bonds).**FIGURE 2.** Plot of  $\Delta_{\text{inductive}}$  calculated at G3(MP2)//B3LYP versus an attenuation factor of  $1.75^{-2n}$  ( $n =$  number of double bonds).**TABLE 4.** Inductive Difference Between Vinyl and Ethyl for the Triplets using eq 4

$n$	B3LYP/6-311+G(3df,2p)// B3LYP/6-31G(d) + ZPE at B3LYP/6-31G(d) (kcal/mol)	G3(MP2)//B3LYP (kcal/mol)
1	-0.105	0.977
2	-0.088	0.988
3	0.005	0.918

the magnitude of the inductive destabilization of the carbene center by vinyl relative to ethyl. It is now possible to correct the advantage of ethyl over vinyl in eq 1. This provides a value of 9.2 (8.9) kcal/mol for the resonance energy of singlet vinylcarbene.

Moving to a consideration of triplet vinylcarbene, the stabilization energy revealed by evaluation of equation 1 for the triplet case is 13.9 kcal/mol at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) with ZPE included at B3LYP/6-31G(d) or 11.7 kcal/mol at G3//B3LYP (Table 3). The inductive effect can be corrected for using isodesmic eq 4. The results are provided in Table 4. Linear plots are problematic, but it appears the inductive effect is small, probably  $\Delta_{\text{inductive}}$  is in the range of 0–1 kcal/mol. Correction for the inductive effect would lead us to a value for the resonance energy of 11–14 kcal/mol.

The values for the resonance energies of singlet and triplet vinylcarbenes, corrected for inductive effects, 8.9–9.2 kcal/mol and 11–14 kcal/mol, respectively, seem very reasonable when compared with related intermediates. One might expect the singlet vinylcarbene to be most closely related to the allyl cation. The results of Barbour and Karty (20–22 kcal/mol),<sup>2b</sup> Mo and Peyerimhoff (55.7 kcal/mol), and Mo et al. (44.7 kcal/mol)<sup>2d</sup> all point to the significance of the resonance energy of the cation. Persuaded by the discussion of Barbour and Karty and adopting their value as the most reasonable assessment, the resonance energy of the singlet vinylcarbene is reduced to a little less than one-half. This reduction fits the picture visualized from the resonance set for vinylcarbene which involves charge separation, which contrasts

with that for allyl cation which exhibits charge delocalization with no charge separation. The more substantial resonance energy for triplet vinylcarbene, relative to the singlet, is consistent with the anticipated delocalization without charge separation. The magnitude at 11–14 kcal/mol is reasonably close to the resonance energy values provided by Barbour and Karty (16–18 kcal/mol),<sup>2b</sup> Mo et al. (28.4 kcal/mol),<sup>2d</sup> Gobbi and Frenking (12.6 kcal/mol),<sup>2e</sup> and Golden, Gac, and Benson (9.6 kcal/mol)<sup>3</sup> for the allyl radical, suggesting that the two intermediates are closely related.

**Acknowledgment.** Support from the MRF fund is gratefully acknowledged.

**Supporting Information Available:** Tables providing energies, zero-point energies, and Cartesian coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO802191M