JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2001; **14:** 847–853
DOI:10.1002/poc.420

Tetraalkylalkene vertical ionization potentials revisited

Stephen F. Nelsen* and Laurie A. Reinhardt

Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706-1396, USA

Received 20 March 2001; revised 25 May 2001; accepted 30 May 2001

ABSTRACT: The vertical ionization potentials for three tetra-α-branched-alkyl-substituted alkenes (**13–15**) are reported, compared with literature data for other tetralkylalkenes, and the values discussed with reference to AM1 semiempirical and B3LYP density functional calculations. Copyright © 2001 John Wiley & Sons, Ltd.
Additional material for this paper is available from the epoc website at http://www.wiley.com/epoc

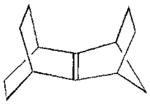
KEYWORDS: tetraalkylalkenes; vertical ionization potentials

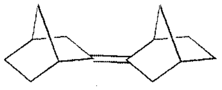
INTRODUCTION

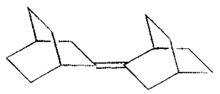
The groups of Houk[1] and of Brown[2] measured vertical ionization potentials (vIP) for tetraalkylalkenes **1–12** and **16** (Scheme 1) using photoelectron spectroscopy and considered the origin of the differences in vIP that were observed.

RESULTS

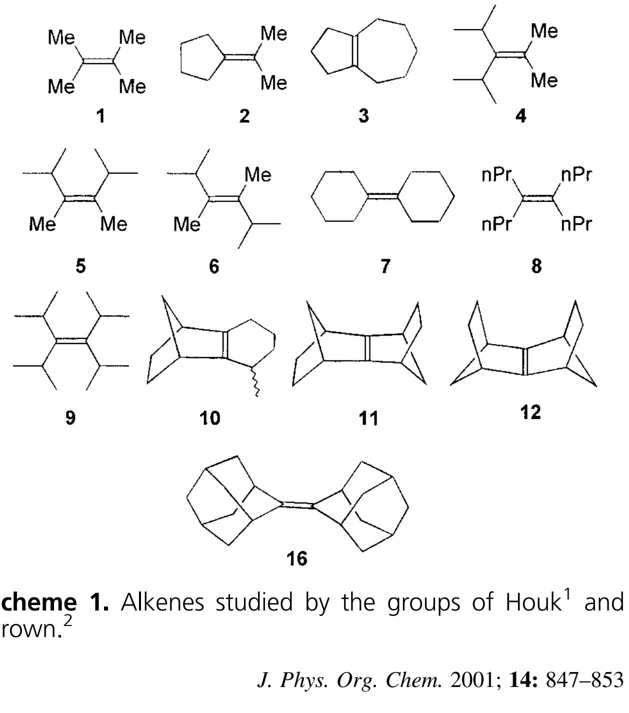
In this work, we measured the vIP values for three tetra-α-branched-alkyl-substituted alkenes, **13–15**. The McMurray reaction[3] was used to prepare **14** and **15** from the related ketones. All four stereoisomers of 2,2′-binorbornylidene and both the *cis* and *trans* isomers of 2,2′-bibicyclooctene were obtained. The major product of the latter reaction was the more stable *trans* isomer[4] **15**, which had a lower R_f value in chromatographic separation, both bridgehead hydrogens upfield and the allylic methylene downfield of the *cis* isomer. That **15** is *trans* was proved both by NOE effects in the NMR spectrum and by obtaining an x-ray crystal structure. The major isomer obtained in the former reaction was **14**, which had the same R_f and chemical shift patterns relative to its other isomers as **15**, and was demonstrated to have *syn* methylene bridges by giving an epoxide upon reaction with *m*-chloroperbenzoic acid that has seven carbon signals. The vIP values for **13–15** appear along with the previously reported compounds in Table 1. Our group previously re-ran the PE spectrum of **16**[5] (we note that using the Ref. 1 vIP for **16** (0.08 eV larger than ours) makes its point in Fig. 1 fall much nearer the correlation line), obtaining a 0.08 V lower vIP than did Houk and co-workers, and the entries in Table 1 use our value, which was obtained and analyzed in the same way as for **13–15**.


13


14


15

Brown *et al.*[2] discussed the data considering a plot of vIP versus the number of carbons. We pointed out later that although changes in vIP for the pure p-hybridized



Scheme 1. Alkenes studied by the groups of Houk[1] and Brown.[2]

---

*Correspondence to: S. F. Nelsen, Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706-1396, USA.
E-mail: nelsen@chem.wisc.edu
Contract/grant sponsor: National Science Foundation; *Contract/grant number:* CHE-9417946; *Contract/grant number:* CHE-9988727.

Table 1. Ionization potential data for tetraalkylalkenes

Compound	Structure	No. of Cs (n_{eff})	vIP (ΔvIP)[a]	vIP [AM1] (obs. − calc.)	vIP [DFT][b] (obs. − calc.)
			Acyclic and monocyclic alkyl groups—		
1	$Me_2C{=}CMe_2$	6 (4.00)	8.46[c] (0.00)	8.45 (−0.01)	
2	$r5{=}CMe_2$	8 (6.00)	8.34[d] (0.00)	8.46 (+0.12)	
3	7/5	10 (7.48)	8.25[d] (0.00)	8.27 (+0.02)	
4	$i\text{Pr}_2\text{CCMe}_2$	10 (7.74)	8.28[c] (0.04)	8.40 (+0.12)	
5	*c*-iPrMeC)$_2$	10 (7.74)	8.27[c] (0.03)	8.38 (+0.11)	
6	*t*-*i*PrMeC)$_2$	10 (7.74)	8.24[c] (0.00)	8.38 (+0.14)	7.96 (−0.28)
7	r6=r6	12 (8.96)	8.16[d] (0.00)	8.37 (+0.21)	
8	*n*Pr$_2$C)$_2$	14 (9.92)	8.11[d] (0.01)	8.39 (+0.28)	
9	*i*Pr$_2$C)$_2$	16 (11.48)	8.13[c] (0.13)	8.38 (+0.25)	
			Bi- and polycyclic alkyl groups—		
10	21/6 (α-Me)	12 (9.74)	8.15[d] (0.3)	8.17 (+0.02)	
11	*a*-21/21	12 (9.74)	7.90[d] (−0.22)	7.96 (+0.06)	7.52 (−0.38)
12	*s*-21/21	12 (9.74)	8.12[d] (0.00)	8.07 (−0.05)	7.74 (−0.38)
13	21/22	13 (10.61)	7.88[e] (−0.18)	8.14 (+0.30)	7.44 (−0.44)
14	221)$_2$	14 (9.74)	7.96[e] (−0.16)	8.36 (+0.40)	7.67 (−0.29)
15	222)$_2$	16 (11.48)	7.95[e] (−0.06)	8.20 (+0.25)	7.52 (−0.43)
16	AdAd	20 (13.90)	7.76[f] (−0.11)	8.21 (+0.45)	7.49 (−0.27)

[a] ΔvIP = vIP − vPI(regr.), where vIP(regr.) = $8.70 - 0.06n_{eff}$.

[b] (U)B3LYP/6–31 + G* calculation.

[c] From Ref. 1.

[d] From Ref. 2.

[e] This work.

[f] From Ref. 4 Allinger MM2 calculations[4] get the *trans* isomer to be 0.90 kcal/mol more stable than the *cis* isomer, while AM1 calculates get it to be 0.26 kcal/mol more stable. Houk's group obtained 7.84 eV.[1]

lone pairs of halogen-containing compounds are quite regular as the number of carbons in the alkyl substituents is increased, vIP does not correlate linearly with the number of carbon atoms, but also depends upon their connectivity[6] (the increments summed to produce n_{eff} are $\alpha = 1.00$, $\beta_1 = 1.00$, $\beta_2 = 0.87$, $\beta_3 = 0.77$, $\gamma_1 = 0.48$, $\gamma_2 = 0.46$, $\delta_1 = 0.25$, $\delta_2 = 0.17$, $\varepsilon_1 = 0.06$; the subscripts refer to first, second, etc., carbon of the given type). Linear decreases in vIP are found for plots versus the 'effective number of carbons,' n_{eff}, for saturated alkyl substituents attached to a more easily ionized center bearing p-orbital electrons. The n_{eff} values are obtained from changes in p-lone pair vIP for alkyl iodides and bromides, and expressed as increments for carbons α, β, γ, etc. to the center, with slightly decreasing increments for a second or third such carbon.[4] Studies of ethers showed that cyclic and bicyclic alkyl groups can also be included (we break rings as symmetrically as possible in calculating n_{eff}).[6]

DISCUSSION

Figure 1 shows a plot of vIP versus n_{eff} for the compounds in Table 1. The lines drawn show a linear correlation, vIP(regr.) = $8.70 - 0.06n_{eff}$, that is excellent for several of these compounds, along with dashed lines 0.03 eV above and below this line so that compounds that deviate significantly may be more easily seen (the reproducibility of vIP values measured by photoelectron spectroscopy appears typically to be about 0.03 eV). The higher n_{eff} compounds deviate the most from the line, with **9** lying above it and **11** and **13–16** lying below it.

The double-headed arrow in Fig. 1 highlights the most surprising result,[2] the 0.22 eV difference in vIP for the two diastereomers of sesquinorbornene, the *anti* isomer **11** (*a*21/21), and *syn* isomer **12** (*s*21/21), which is strikingly large for compounds of the same connectivity and has been much discussed. Brown and co-workers attributed the low vIP for **11** to exceptionally large σ,π interactions destabilizing the π orbital of this nearly planar alkene relative to the pyramidalized **12**.[2] The double bond of **12** is pyramidalized in the direction making its two-carbon bridges approach instead of its

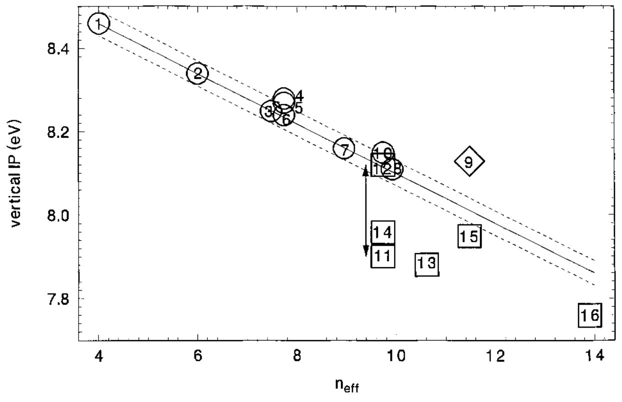
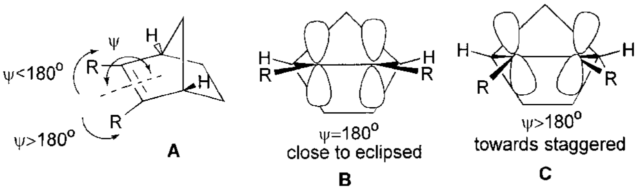


Figure 1. Plot of vIP versus n_{eff} for the compounds in Table 1



Scheme 2. Geometry relationships in sesquinorbornenes

one-carbon bridges. The latter would lead to less β-carbon non-bonded interaction because the one-carbon bridge is bent further away from the $C_bC{=}CC_b$ plane than are the two carbon bridges. To allow consideration of both directions of bend, we call the angle between the two $C_bC{=}CC_b$ planes (C_b refers to a bridgehead carbon) of bis(C,C′-bicyclic) alkenes ψ, and use $\psi < 180°$ when the substituents on norbornyl systems are pyramidalized toward the one-carbon bridge and $\psi > 180°$ when they are pyramidalized toward the two-carbon bridge (Scheme 2). Using this nomenclature, derivatives of **11** have ψ values near 180°, but those for **12** derivatives are 196–198°,[7] and this large difference in pyramidalization is clearly important in causing their vIP values to be so different. Houk and co-workers give the most detailed analysis of the reasons for ψ not being 180° for **12**.[8] Both the unusual bond angles about the double bond (the small C_b—C=C angles make the $C_bC_vC_b$ bond angle very large) and the unusually electron rich π orbital (because of the four α-branched substituents) in sesquinorbornenes lower the out-of-plane bending force constants. As indicated in structures **A** and **B**, the large α-branched substituents on each norbornene ring are nearly eclipsed with the bridgehead CH bonds when $\psi = 180°$. The *syn* compound **12** stabilizes itself by bending substantially to stagger the substituents, as indicated in **C** (Houk and co-workers showed the slightly less familiar 'two-membered ring' cartoons of the π bonds in the projections **B** and **C**; we show π bond representations, which lead to the same conclusions and are more familiar to most of us). The *anti* compound **11** does not get any eclipsing relief upon pyramidalization because what stabilizes one ring destabilizes the other by the same amount, so it remains at $\psi = 0$ despite having a small bending force constant. The present work demonstrates that the 21/22 system **13** has a vIP close to that for **11**. However, derivatives of **11** are nearly planar and the one derivative of **13** studied by crystallography has a ψ of 198°, which is as pyramidalized, and also is pyramidalized in the same direction as **12**.[9] If **12** has a higher vIP than **11** because it is pyramidalized, why does **13** have a vIP close to that of **11**, and not that of **12**?

We carried out quantum mechanical calculations to try to understand these results. We calculated vIP by subtracting the enthalpy calculated for the geometry optimized neutral compound ($\mathbf{n}^0$) from that obtained by a single point calculation of the cation using the geometry of the neutral compound ($\mathbf{n}^+$). The second to last column of Table 1 shows vIP values calculated by AM1.[10] (our AM1 calculations were carried out using various versions of Clark's program VAMP)[11]. AM1 calculations give larger vIP than the observed value in all cases but **1**, and the amount usually increases with n_{eff}. We note that the effect of α-branching on lowering vIP appears to be underestimated by AM1 calculations. AM1 calculations are very rapid (<25 s of CPU time were required for geometry optimization of each compound discussed here) and have proven especially useful for understanding the effects of ring size changes on the properties of bis(*N*,*N*′-bicyclic) hydrazines.[12] Although errors in vIP as large as 0.45 eV occur for some of the higher n_{eff} compounds in Table 1, when the geometry is changed for a molecule, or when diasteromers are compared, such errors tend to cancel, and greater accuracy is expected for such changes than for comparing molecules that differ more in structure. Employing these rapid calculations allows the investigation of effects of changing geometry that would take too long to be worthwhile by more sophisticated calculation methods, because such calculations would take months instead of hours of CPU time to carry out. For example, it took us 3.7×10^3 times as much CPU time to optimize **15** using B3LYP/6–31G+* calculations as using AM1 (that is, over 25 h versus 24 s), and 2.4×10^4 times as long to do the single point on the cation at UB3LYP/6–31G+* (that is, over 10 h versus 1.5 s), even though a more powerful machine was used for the Gaussian calculations. The last column of Table 1 contains results of density functional theory (DFT) calculations of vIP carried out at the (U)B3LYP/6–31G+* level using Gaussian 98.[13] The ψ angles obtained are **11** 180.0°, **12** 195.5° and **13** 191.2°, so the pyramidalities of these sesquibicyclic alkenes obtained using B3LYP/6–31G+* optimizations are certainly better than those from AM1 calculations, which gave ψ far too close to 180° for **12** (183°) and **13** (181.4°). Both methods of calculation show the 2,2-bicyclic compounds **14** and **15** to be untwisted at their double bonds, as expected. However, surprisingly to us, the DFT vIP values are often significantly further from experiment than are the AM1 values (see Table 1). There are no spin contamination problems; the $\langle S^2 \rangle$ values for the $\mathbf{n}^+$ structures are ≤ 0.754 in all cases. The difference between the DFT vIP values for the *anti* and *syn* 21/21 systems is the experimental value, much better performance than AM1, as expected because the AM1 pyramidalities were wrong. It seems that this DFT method substantially overestimates the effect of α-branching lowering vIP. It does not appear to us to be reasonable to state that DFT calculations are likely to help one understand the ionization potentials any better than the AM1 calculations, and we use values calculated by AM1 in this discussion. The DFT calculations are too slow to make carrying out the calculations discussed below reasonable.

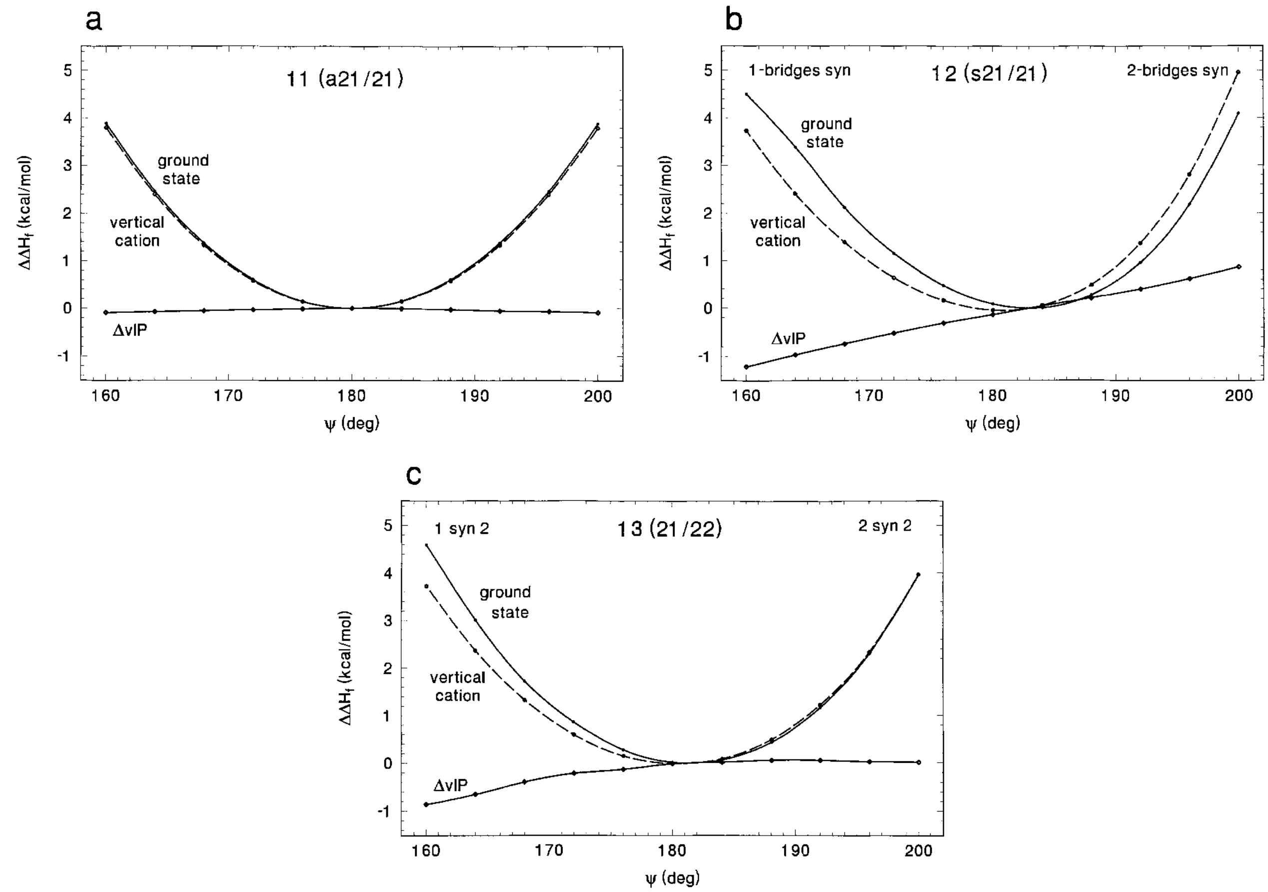
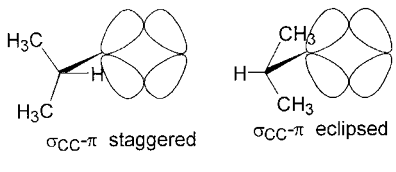


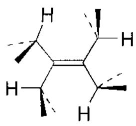
Figure 2. Plots of ΔvIP calculated by AM1 and its components, $\Delta\Delta H_f(\mathbf{n}^+)$ (labeled vertical cation) and $\Delta\Delta H_f(\mathbf{n}^0)$ (labeled ground state) as a function of pyramidality measured by ψ for (a) **11**, (b) **12** and (c) **13**

Figure 2 shows the changes in vIP as a function of ψ and also its $\Delta\Delta H_f(\mathbf{n}^+)$ and $\Delta\Delta H_f(\mathbf{n}^0)$ components for **11–13**. Vertical ionization potentials are often discussed in terms of stabilization or destabilization of the π orbital from which ionization occurs, because Koopmans' theorem works so well for ionization potentials. However, vIP is the difference in enthalpy between the vertical cation ($\mathbf{n}^+$) and the neutral ground state ($\mathbf{n}^0$). Effects that stabilize both the cationic and neutral oxidation states will affect vIP, and effects on the two oxidation states are calculated to be different. These plots rationalize nicely why vIP is larger for **12** than for **11**, yet similar for **11** and **13**. Changing ψ in either direction from 180° increases s hybridization, which alone would cause an increase in vIP. However, pyramidalization also changes the overlap between the π and σ framework orbitals in a rather complex fashion. The sum of all effects results in a very small decrease in vIP as ψ deviates further from 180° for **11** [*a*21/21, see Fig. 2(a)]. In contrast, for **12** [*s*21/21, Fig. 2(b)] vIP increases significantly as ψ increases on either side of 180°, because $\Delta\Delta H_f(\mathbf{n}^+)$ increases relative to $\Delta\Delta H_f(\mathbf{n}^0)$ as the alignment of the p-orbital axes with the 1-bridge σ-bonds becomes poorer and poorer (see structure **C**). This suggests that radical cation C_1-bridge/σ,π^+ interaction dominates the pyramidality change effect. Pyramidalizing **13** (21/22) to more positive ψ raises vIP in the 160–170° region almost as much as it does for **12**, but the effect levels out in the more positive ψ region, as the interactions with the single one-carbon bridge become small. Thus pyramidalization is not predicted to raise vIP for **13**. Although AM1 gives a significantly larger error in vIP for **13** than for either **11** or **12**, we suggest that the trends upon pyramidalization of these compounds help in understanding the vIP pattern observed.

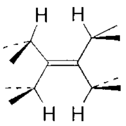
The next most striking thing about Table 1 and Fig. 1 is the similarity of vIP for **8** and **9**, which is not expected because α-branching significantly decreases vIP, so that the observed oxidation potential for **9** is actually about 0.13 eV higher than expected by comparing its vIP with those of other tetraalkylalkenes. This caused us to



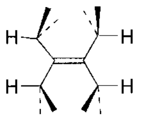
Scheme 3. Staggered (S) and eclipsed (E) conformations for isopropyl groups



9(ESES)



9(SSSS)



9(EEEE)

consider how large the effect is for having isopropyl groups oriented staggered with respect to a C=C bond versus having them eclipsed, as shown in cartoon form in Scheme 3 using the 'two-membered ring' cartoon for a π bond used by Houk *et al.*[8a] It is known that **9** assumes a conformation with each isopropyl group α-hydrogen tucked between the methyls of an adjacent isopropyl group, the conformation labeled ESES (for alternating eclipsed and staggered substitutents),[14] and that AM1 as well as molecular mechanics calculations do a reasonable job of describing the energy surface for twisting.[14d,e] The vIP calculated for ESES **9** is indeed substantially higher than that for the SSSS and EEEE rotamers (see Table 2), but this may well occur because the latter are so crowded that they are calculated to have significant twisting about the C=C bond (SSSS **9** has 14° twist and EEEE **9** has 24° twist).

Although a significant decrease in vIP occurs as staggered isopropyl groups are rotated to become eclipsed in the least hindered system examined, the dialkyl *t*-*i*PrHC=)$_2$, such an effect was not calculated for the tetraalkyl cases **4**–**6**, and an increase is found for **6** using DFT. It seems clear that calculations at a level that predicts vIP better than those examined would have to be carried out to consider whether there is a significant E versus S effect on vIP in acyclic compounds. We note that neither DFT nor AM1 calculations predict the similar ΔvIP observed for the SSSS bis(bicyclic) compounds **14** and **15**, and do not appear to us to give insight as to why **14** and **16** fall well below the correlation line but **15** falls rather near it.

CONCLUSIONS

The vIP values for **11**–**13** provide excellent examples of the fact that deforming from an equilibrium geometry can have different effects upon the neutral form and the vertical cation, and that both oxidation states need to be considered in analyzing vertical ionization potentials. The rather poor absolute performance of B3LYP calculations for calculating the vIP values of these alkenes was not expected, and it suggests that despite their good performance for geometries,[15] DFT calculations may not be the best to use for estimating internal reorganization energies (Marcus's λ_{inner}), which is calculated from the energies of $\mathbf{n}^0$, $\mathbf{n}^+$ and both oxidation states at the relaxed cation geometry.[16] According to AM1 calculations, pyramidalizing to ψ <180° for **12** (*s*21/21) is calculated to lower vIP because the vertical cation is less destabilized than the neutral form due to overlap with the 1-carbon bridges improving, whereas pyramidalizing to ψ >180° raises vIP because it destabilizes the vertical cation more than the neutral form owing to overlap with the 1-carbon bridges becoming less favorable, combined with the increase in s-hybridization that occurs for both directions of bend. The behavior of **13** (21/22) shows that it is principally overlap with the 1-carbon bridges that matters, because the shape is similar to **12** at ψ <180°, but for ψ >180°, where overlap with the 1-carbon bridge is poor, neutral and cation are destabilized by nearly the same amount, and vIP no longer varies as ψ is increased. For **11** (a21/21), where changing ψ from 180° in either direction improves overlap with one 1-carbon bridge but makes it

Table 2. AM1-calculated relative vertical ionization potentials and their components for some isopropyl-substituted alkenes

Compound	*i*Pr	$\Delta\Delta H_f(\mathbf{n}^0)$ (kcal mol^{-1})	$\Delta\Delta H_f(\mathbf{n}^+)$ (kcal mol^{-1})	ΔvIP (eV)
*i*Pr$_2$C=)$_2$ (**9**)	ESES	0	0	0
	SSSS	2.98	−0.21	−0.12
	EEEE	17.60	12.00	−0.24
t-*i*PrHC=)$_2$	SS	0	0	0
	ES	1.37	−2.09	−0.15
	EE	2.72	−0.97	−0.16
*i*Pr$_2$C=CMe$_2$ (**4**)	ES	0	0	0
	SS	1.03	0.83	−0.01
	EE	2.67	2.98	+0.01
c-*i*PrMeC=)$_2$ (**5**)	SS	0	0	0
	ES	2.13	2.85	+0.03
	EE	8.62	9.10	+0.02
t-*i*PrMeC=)$_2$ (**6**)[a]	SS	0 (0)	0 (0)	0 (0)
	ES	2.05 (2.71)	2.05 (3.40)	0.00 (+0.03)
	EE	4.33 (5.13)	4.34 (6.20)	0.00 (+0.05)

[a] The numbers in parentheses are from (U)B3LYP/6–31+G* calculations.

poorer with the other, vIP is nearly unaffected by the size of ψ in the range studied because destabilization of both oxidation states is the same.

EXPERIMENTAL

*Tetracyclo[6.2.2.$1^{3,6}$.$0^{2,7}$]tridec-2,7-ene (**13**).* This was prepared by the literature method.[17]

*syn-trans-2-Bicyclo[2.2.1]hept-2-ylidenebicyclo[2.2.1]-heptane (**14**).* A solution of $TiCl_3$ (22 g, 0.145 mol) in anhydrous THF (200 ml) was stirred at room temperature. Li wire (3 g, 0.44 mol), cut into small pieces, was added and the mixture refluxed for 1 h. After cooling, bicyclo[2.2.1]heptan-2-one[18] (4 g, 0.036 mol) in anhydrous THF (50 ml) was added dropwise via a canula. The reaction mixture was refluxed for 10 h. After cooling, the reaction mixture was diluted with pentane (100 ml) and carefully filtered through a pad of Fluorosil in a sintered-glass funnel. Rotary evaporation of the solvent gave 1.4 g (20%) of a colorless liquid. ^1H NMR showed a mixture of the four possible isomers. Purification was accomplished by preparative TlC on silica plates (Merck) impregnated with $AgNO_3$ using hexane–diethyl ether (99:1) as eluent. The *trans* configuration for **14** was inferred by analogy with **15**, as it had a larger yield, smaller R_f (0.23) and bridgehead hydrogens upfield of, and allylic methylene downfield of the other isomers. The one-carbon bridges being *syn* was established by epoxidation with *m*-CPBA, which produced a compound having seven ^{13}C resonances as the major product. ^1H NMR ($CDCl_3$): δ 2.53 (br s, 2H), 2.30 (br s, 2H), 2.11 (d, $J = 15$ Hz, 2H), 1.69 (d, $J = 15$ Hz, 2H), 1.6–1.5 (series of m, 4 H), 1.36–1.11 (series of m, 8 H). ^{13}C NMR ($CDCl_3$): δ 131.51 (C_q), 41.0 (CH), 39.03 (CH_2), 37.17 (CH_2), 36.77 (CH), 29.08 (CH_2), 28.59 (CH_2). HRMS: *m/z* 188.1574 (M, 51%) observed, 188.1565 calculated for $C_{14}H_{20}$.

*trans-2-Bicyclo[2.2.2]oct-2-ylidenebicyclo[2.2.2]octane (**15**).* A solution of $TiCl_3$ (5 g, 0.033 mol) in anhydrous THF (30 ml) was stirred at room temperature. Li wire (0.067g, 0.1 mol), cut into small pieces, was added and the mixture refluxed for 1 h. After cooling, bicyclo[2.2.2]octan-2-one[19] (1 g, 0.008 mol) in anhydrous THF (20 ml) was added dropwise via a canula. The reaction mixture was refluxed for 20 h. After cooling, the reaction mixture was diluted with pentane (30 ml) and carefully filtered through a pad of Fluorosil in a sintered-glass funnel. Rotary evaporation of the solvent gave 0.43 g (25%) of a white solid. ^1H NMR showed the ratio of *trans* to *cis* olefins was 2:1. Fractional sublimation provided a pure sample of the *trans* compound; m.p. 126–127 °C. ^1H NMR ($CDCl_3$): δ 2.3 (br s, 2H), 2.13 (d, 4H), 1.66 (br s, 2H), 1.51–1.45 (series of m, 16 H). ^{13}C NMR ($CDCl_3$): δ 129.65 (C_q), 33.46 (CH_2), 27.86 (CH), 26.37 (CH), 25.93 (CH_2), 25.91 (CH_2). HRMS: *m/z* 216.1884 (M, 100%) observed, 216.1878 calculated for $C_{16}H_{24}$. Double bond configuration was demonstrated by NOE: for **15** irradiation at either δ 2.3 (allylic) or 1.66 (non-allylic) bridgehead hydrogens led to ~4% NOE of the allylic CH_2 protons at δ 2.13. For the minor isomer, irradiation of the non-allylic bridgehead (δ 1.76) led to ~3.5% NOE of the allyic CH_2 proton signal, but irradiation of the allylic bridgehead signal (δ 2.46) signal led to <1% NOE. Therefore, **15** is the *trans* double bond isomer. A later crystal structure determination verified this conclusion (shown in detail in the PhD Thesis of L.A.R).

Photoelectron spectra. Spectra were run on a Varian IEE-15 spectrometer, modified with a rebuilt analyzer, and flowing He I lamp ionization source. Peak potentials were estimated by superimposing sums of Gaussian curves of adjustable position, width and intensity over the unsmoothed data points on the screen of an IBM-PC-XT, using software written by P. A. Petillo. The spectra and fitted curves are illustrated in the PhD Thesis of L.A.R.

Acknowledgements

We thank the National Science Foundation for partial financial support of this work under grants CHE-9417946 and -9988727, and the National Science Foundation, National Institutes of Health, Intel Corporation and the University of Wisconsin for departmental equipment grants used for the spectrometers and computers (NSF CHE-9522057) employed. Special thanks are due to Timothy Clark for providing the VAMP programs used for carrying out the AM1 calculations and to Frank Weinhold for assistance with the Gaussian calculations.

REFERENCES

1. Mollere PD, Houk KN, Bomse DS, Morton TH. *J. Am. Chem. Soc.* 1976; **98**: 4732.
2. Brown RS, Buschek JM, Kopecky KR, Miller AJ. *J. Org. Chem.* 1983; **48**: 3692.
3. McMurray JE. *Chem. Rev.* 1989; **89**: 1513.
4. Allinger NJ. *J. Am. Chem. Soc.* 1977; **99**: 8127; Allinger NL, Yuh Y. *QCPE* 1980; **12**: 395; Profeta S. *QCPE Bull.* 1981; **1**: 57.
5. Nelsen SF, Klein SJ, Trieber DA II, Ismagilov RF, Powell DR. *J. Org. Chem.* 1997; **62**: 6539.
6. Nelsen SF. *J. Org. Chem.* 1984; **49**: 1891.
7. Watson WH, Galloy J, Bartlett PD, Roof AM. *J. Am. Chem. Soc.* 1981; **103**: 2022.
8. (a) Houk KN, Rondan NG, Brown FK, Jorgensen WL, Madura JD, Spellmeyer DC. *J. Am. Chem. Soc.* 1983; **105**: 5980; (b) Houk KN, Rondan NG, Brown FK. *Isr. J. Chem.* 1983; **23**: 3.
9. Paquette LA, Carr RVC, Charumilind P, Blount JF. *J. Org. Chem.* 1980; **45**: 4922.
10. Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP. *J. Am. Chem. Soc.* 1985; **107**: 3902.
11. Rauhut G, Chandrasekhar J, Alex A, Steinke T, Clark T. VAMP 5.0, Oxford Molecular, Oxford, 1994.
12. (a) Nelsen SF, Blackstock SC, Kim Y. *J. Am. Chem. Soc.* 1987; **109**: 677; (b) Nelsen SF, Frigo TB, Kim Y, Blackstock SC. *J. Am.*

Chem. Soc. 1989; **111**: 5387; (c) Nelsen SF, Tran HQ, Ismagilov RF, Chen L-J, Powell DR. *J. Org. Chem.* 1998; **63**: 2536.

13. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Jr., Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA. Gaussian 98, Revision A.9. Gaussian: Pittsburgh, PA, 1998.
14. (a) Langler RF, Tidwell TT. *Tetrahedron Lett.* 1975; 777; (b) Bomse DS, Morton TH. *Tetrahedron Lett.* 1975; 781; (c) Casalone G, Pilati T, Simonetta M. *Tetrahedron Lett.* 1980; **21**: 2345; (d) Ermer O. *Angew. Chem. Int. Ed. Engl.* 1983; **22**: 998; (e) Nelsen SF, Chen L-J, Powell DR, Neugebauer FA. *J. Am. Chem. Soc.* 1995; **117**: 11434.
15. Blomgren F, Larsson S, Nelsen SF. *J. Comput. Chem.* 2001; **22**: 655.
16. Nelsen SF, Blackstock SC, Kim Y. *J. Am. Chem. Soc.* 1987; **109**: 677.
17. (a) De Lucchi O, Piccolrovazzi N, Licini G, Modena G, Valle G. *Gazz. Chim. Ital.* 1987; **117**: 401; (b) De Lucchi O, Piccolrovazzi N, Modena G. *Tetrahedron Lett.* 1986; **27**: 4347.
18. Kleinfelter DC, Schleyer PvR. *Org. Synth. Coll. Vol.* 1973; **5**: 852.
19. (a) Walborsky HM. *J. Am. Chem. Soc.* 1961; **83**: 988; (b) Roche VF, Roche EB, Nagel DL. *J. Org. Chem.* 1982; **47**: 1368.