J. Am. Chem. Soc. 1992, 114, 6484-6486

4 are the ones most consistent with the ESR spectra recorded at low temperatures. Unfortunately, the binding energies indicate all of the possible isomer complexes to be unstable relative to the separated Al and benzene. Structures 2 and 4 both involve extensive distortion of the benzene ligand, and the complex binding energies are perhaps being underestimated because a much higher quality calculation is needed to compute the benzene distortion energy accurately. We have performed single point calculations on the isolated benzene ligands held at the different optimal complex geometries using larger basis sets which included polarization functions on the C and H but found little change in the benzene distortion energy. These large Al-benzene interactions, which must be taking place in order to cause the benzene to distort, suggest to us one further reason to favor structures 2 and 4 as being the most likely candidates for the complexes observed in the ESR experiments. The off-center isomer 4 would also have principal moments of inertia similar to those used by Mitchell et al. to estimate the Al-benzene complex binding energy.[9] In the ESR spectra at higher temperatures the Al starts to interact equivalently with all six C atoms. Our calculations provide two possible explanations. First, the planar $C_6H_6^-$ differs by $\sim$5 kcal/mol from the boat form of $C_6H_6^-$, allowing an easy interchange of the C atoms at the out-of-plane positions. Some support of this idea is given by previous work which shows $C_6H_6^-$ to undergo only a slight Jahn-Teller distortion giving rise to an ESR spectrum with six equivalent protons.[26] The alternative is that the Al on-top structure, 3, is a transition state interconnecting two Al σ-bridging structures with different out-of-plane C atoms. Structures 2, 3, and 4 have similar C-C bond length alternations, and for this reason we do not expect the on-top structure, 3, to serve as a transition state between different π-bridging structures 5.

The on-top structure, 3, is also interesting in its own right as it may be the prototypical structure formed when Al adsorbs on graphite. In our earlier Al on graphite cluster calculations we kept the positions of the C atoms rigidly fixed. The energetic demands for C honeycomb on the graphite surface to distort into a boat must be prohibitive. However, allowing a single C atom to move out of the surface plane is more reasonable. This is essentially what has happened in structure 3; the bond order between the out-of-plane C and Al suggests that a fairly strong Al-C bond is formed while the remaining benzene C atoms stay close to planar. Srivastava and Almlöf found a similar out-of-plane distortion when they performed calculations on the three-membered-ring compound $AlC_{13}H_9$.[27] In their optimum structure they found the central C to be 0.5 Å out-of-plane and the C-Al distance to be 2.1 Å, which is very similar to what we find for structure 3. A number of adsorbate-induced surface reconstructions have now been experimentally observed.[28] The Srivastava et al. calculations and our calculations demonstrate that substrate relaxation effects also need to be considered when using clusters to model adsorbate interactions on surfaces.

Conclusion

The Al-benzene complex is theoretically found to be a C-C bridging structure with the benzene ligand distorted into a boat shape. Close in energy is another structure with the Al centered above the benzene boat. In both complexes the Al interacts most strongly with the two out-of-plane para C atoms and the Al-C bonds are of σ type. These two structures are consistent with the low-temperature ESR spectra, which have a hyperfine interaction involving only two equivalent protons. The small barrier of interconversion between the two structures is the most likely explanation for the equivalence of the six protons in the higher temperature 220 K ESR spectrum. Our calculations do not provide support for an Al π-bridging complex being observed.

We have also found an on-top structure where the Al atoms bonds directly above a C atom. The on-top structure may be prototypical for Al chemisorbing on graphite and involve surface relaxation of the C substrate.

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(26) Burrow, P. D.; Modelli, A.; Jordan, K. D. *Chem. Phys. Lett.* **1986**, *132*, 441. Birch, A. J.; Hinde, L.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 3370.

(27) Srivastva, S.; Almlöf, J. *Surf. Sci.* **1991**, *255*, L509.

(28) (a) Somorjai, G. A.; Van Hove, M. A. *Prog. Surf. Sci.* **1989**, *30*, 201. (b) Christmann, K. *Z. Phys. Chem.* (*Wiesbaden*) **1987**, *154*, 145.

Ab Initio/IGLO Study of Strained Bicyclic Olefins[†]

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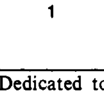
Abstract: The ^{13}C NMR chemical shifts of strained olefins **1**, **2**, **3**, and **6** were calculated using the ab initio/IGLO method(DZ/6-31G*). The calculated values resemble the experimental data closely but show a systematic drift with increased strain. The chemical shifts of the yet unknown olefins **1** and **2** were predicted to be extremely deshielded.

Introduction

Among olefins with colinear π orbital angle vectors[1b] the simplest and most strained symmetrical olefins are bicyclo[1.1.0]but-1,3-ene (**1**), bicyclo[2.1.0]pent-1(4)-ene (**2**), and bicyclo[2.2.0]hex-1(4)-ene (**3**). The former two olefins have been prepared only in the form of the substituted derivatives and characterized by trapping experiments.[2] Casanova and Rogers[3] and Wiberg et al.[3] prepared olefin 3 and studied its reactivity. Ca-



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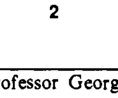

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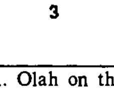

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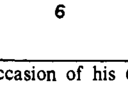

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[†] Dedicated to Professor George A. Olah on the occasion of his 65th birthday.

(1) (a) On leave from California State University, Los Angeles. (b) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137. Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243.

(2) Szeimies, G.; Harnish, J.; Baumgartl *J. Am. Chem. Soc.* **1977**, *99*, 5183. Szeimies-Seebach, U.; Szeimies, G. *J. Am. Chem. Soc.* **1978**, *100*, 3966. Harnisch, J.; Baumgartl, O.; Szeimies, G.; Van Meerssche, M.; Germain, G.; Declercq, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 3370.

(3) Wiberg, K. B.; Burgmaier, G. J.; Warner, P. *J. Am. Chem. Soc.* **1971**, *93*, 246. Wiberg, K. B.; Bailey, W. F.; Jason, M. *J. Org. Chem.* **1974**, *93*, 246. Casanova, J.; Rogers, H. J. *J. Org. Chem.* **1974**, *39*, 3803.

0002-7863/92/1514-6484$03.00/0

Table I. Calculated and Experimental ^{13}C NMR Data for Strained Olefins[a]

olefin	C1	C2	C3	C4	C5	C6	C7	Σδ
cyclopropene[b]	122.9	122.9	−3.5					
	(111.0)	(111.0)	(0.0)					
cyclobutene[b]	143.1	143.1	22.3	2.3				
	(139.5)	(139.5)	(33.7)	(33.7)				
1	455.5	126.1	455.1	126.1				
2	284.5	25.4	25.5	284.5	63.2			
3[c]	172.3	35.6	35.6	172.3	35.6	35.6		
	(163.5)	(43.7)	(43.7)	(163.5)	(43.7)	(43.7)		
6[d] (C_s)	153.5	23.8	17.8	23.8	153.5	21.9	21.9	416.2
(C_{2v})	153.0	23.6	16.7	23.6	153.0	21.6	21.6	413.7
	(150.2)	(32.1)	(27.3)	(32.1)	(150.2)	(28.5)	(28.5)	448.9

[a] Calculated at DZ//6-31G*. The values in parentheses correspond to the experimental values. [b] Experimental values from ref 10. [c] Experimental values from ref 4. [d] Experimental values from ref 6.

sanova and co-workers[4] also succeeded in isolating the pure olefin and obtained its ^1H, ^{13}C NMR, IR, and Raman spectra. Olefin **3** shows ^{13}C absorptions at δ ^{13}C 163.5 and 43.7 for the olefinic and the allylic carbons, respectively. Theoretical ab initio calculations of Wagner, Schleyer, et al.[5a] and Wiberg and co-workers[5b] predict that **3** should exist in the planar D_{2h} conformation.

The ^{13}C NMR chemical shifts of hydrocarbons are indicative of relative hybridization states of the carbons. Among other factors the molecular strain can exert a dominant role on the state of hybridization of the carbons. As the internal strain of the molecules increases, the strained olefinic carbons become increasingly deshielded. This effect was explained as due to the torsionally induced rehybridization.[5c] The olefinic ^{13}C NMR absorptions for dimethylcyclobutene (**4**),[6] bicyclo[4.2.0]oct-1(6)-ene (**5**),[6] bicyclo[3.2.0]hept-1(5)-ene (**6**),[6] and bicyclo[2.2.0]hex-1(4)-ene (**3**)[4] are 136.6, 141.7, 150.2, and 163.5 ppm, respectively, reflecting a gradual increase in ring strain in this series. The corresponding chemical shifts for olefins **1** and **2** would be expected to be even more deshielded. However, because of extreme reactivity, the synthesis and NMR characterization of these olefins remains to be accomplished.

Recently calculation of the ^{13}C NMR chemical shifts by the IGLO (Individual Gauge for Localized Orbitals) method was shown to reproduce experimental values for carbocations, and such data have frequently been used to distinguish the various conformations of a given carbocationic species.[7] Since strained olefins resemble the carbocations in their ground state geometry, the IGLO calculations for these olefins would be expected to closely reproduce the experimental values. Schindler and Kutzelnigg's calculations on cyclobutene and cyclopropene support this expectation.[7]

Results and Discussions

We have carried out IGLO calculations[8,9] on olefins **1**, **2**, **3**, and **6** at the DZ level and the data are shown in Table I. The correlation of the calculated ^{13}C NMR chemical shift data with the known experimental values is excellent. Schindler and Kutzelnigg[8] used experimental geometries of cyclobutene and cyclopropene in calculating the IGLO chemical shifts and obtained chemical shifts slightly deshielded over the experimental values. We also carried out IGLO calculations on cyclobutene and cyclopropene using 6-31G* geometries. The values presently obtained are in even better agreement with experimental results. Figure 1 shows the correlation between the experimental and the IGLO calculated chemical shifts. We found, in accordance with

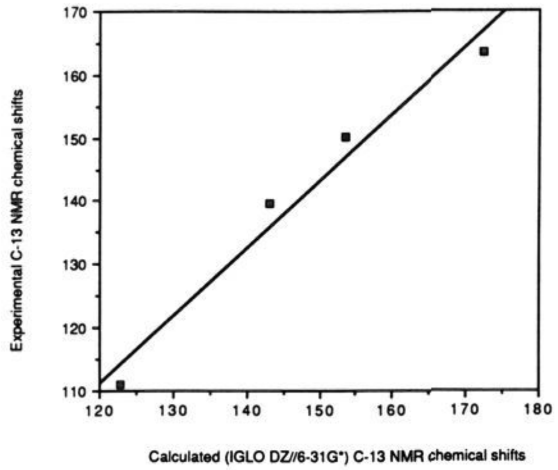

Figure 1. Correlation of experimental and IGLO chemical shifts.

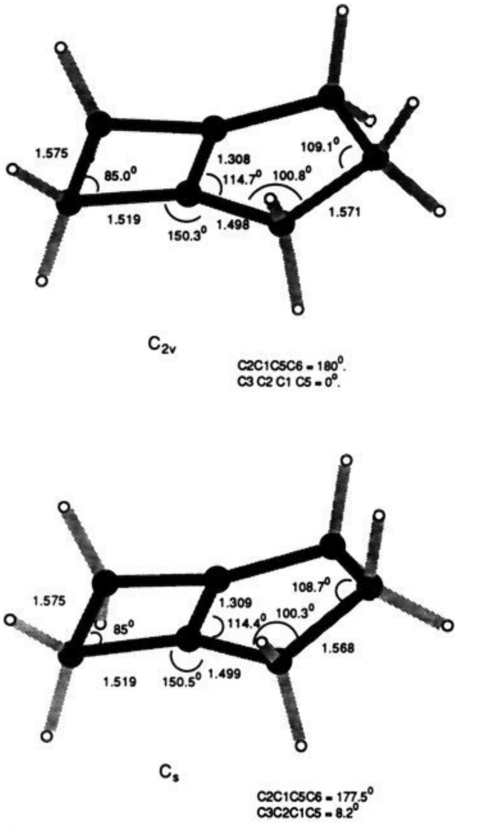

Figure 2. Selected bond lengths, angles, and dihedral angles for C_{2v} and C_s conformers of **6** calculated at 6-31G*.

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(4) Casanova, J.; Bragin, J.; Cottrell, F. D. *J. Am. Chem. Soc.* **1978**, *100*, 2264.

(5) (a) Wagner, H.-U.; Szeimies, G.; Chandrasekhar, J.; Schleyer, P. v. R.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 1210. (b) Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85. (c) Beckenbaugh, W. M.; Wilson, S. R.; Loeffler, P. A. *Tetrahedron Lett.* **1972**, *47*, 4821.

(6) Aue, D. H.; Kos, A. Unpublished results; personal communication.

(7) (a) Schleyer, P. v. R.; Carneiro, J. W. de M.; Koch, W.; Raghavachari, K. *J. Am. Chem. Soc.* **1989**, *111*, 5475. (b) Olah, G. A.; Reddy, V. P.; Rasul, G.; Prakash, G. K. S. *Croat. Chem. Acta* (*Sunko Issue*), in press.

(8) Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1983**, *105*, 1360.

(9) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020 and references cited therein.

(10) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, 1980.

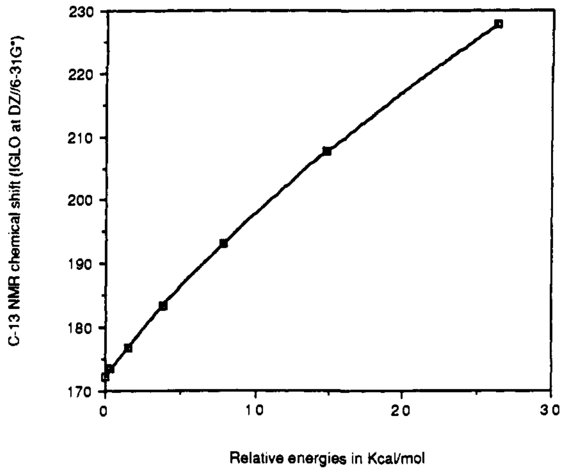

Figure 3. Correlation of ^{13}C NMR chemical shifts (IGLO) with the energies for different C_{2v} conformers, relative to the planar conformation (puckering angles of 0, 10, 20, 30, 40, 50, and 60°) of **3**.

the earlier work of Wagner, Schleyer, et al.[5a] and Wiberg and co-workers,[5b] that the planar conformations of olefins **1** and **2** (D_{2h} and C_{2v}, respectively) were the transition states on the potential energy surface and the bent conformations (C_{2v} and C_s, respectively) were minima, confirmed by frequency calculations at the 6-31G* level. The geometries of the latter conformations were used in the IGLO calculations. Bicyclo[2.2.0]hex-1(4)-ene (**3**) was optimized as the D_{2h} structure at the 6-31G* level and was confirmed as a minimum by frequency calculation at the same level. This geometry was used for the IGLO calculation. Olefin **6** was optimized at 6-31G* for the C_s and C_{2v} conformations. The C_s conformer (HF = −270.82800 hartrees) was found to be more stable than that of C_{2v} (HF = −270.82789 hartrees) only by 100 cal/mol. The geometries thus obtained for the C_s and C_{2v} conformers were used for IGLO calculation. Selected bond lengths, angles, and dihedral angles of these conformers are shown in Figure 2.

From Table I it is evident that the olefinic carbons of olefins **1** and **2** are the most deshielded and are more deshielded than any known olefinic hydrocarbon. Of further significance are the data for olefins **6** and **3**. The close resemblance of the IGLO-calculated chemical shifts to the experimental values supports the D_{2h} geometry, predicted from the Raman and infrared data of matrix-isolated **3**.[4] Thus IGLO calculations augment the geometry calculations by the ab initio methods in predicting the geometries of these molecules. We have also calculated the ^{13}C NMR chemical shifts for olefin **3** at different C_{2v} geometries, all fully optimized at HF/6-31G*. As the pucker angle increased from 0 to 60°, the HF energies of these conformers also systematically increased. The relative energies of these conformers also gradually increase with the corresponding increase in their olefinic ^{13}C NMR chemical shifts (IGLO) (Figure 3), further reflecting the dependence of the ^{13}C NMR chemical shifts on the internal strain of the molecules. The ^{13}C NMR chemical shift values of olefin **3** were also calculated at basis II level (δ ^{13}C: 174.2 (C1, C4), 35.9 (C2, C3, C5, C6)). However, these values although similar are not as close as those for the DZ level with the experimental values. Since the C_s and C_{2v} conformers of **6** differ in energy by only 100 cal/mol, it is not unequivocal to distinguish these two even with IGLO calculations. However, the summation of the chemical shifts for the C_s conformer is slightly higher than that of the C_{2v} conformer and more closely approaches the experimental value (Table I). On this basis, we assign the preferred conformer of **6** as C_s.

Method, Basis Set, and Geometry

IGLO calculation were performed according to the reported method.[8,9] Huzinaga[11] Gaussian lobes for the DZ basis set are as follows:

C: 7s 3p contracted to [4111, 21]

H: 3s contracted to [21]

Geometries of the olefins were optimized at the 6-31G* level by using the Gaussian-86[12] series of programs on an Alliant FX/40 computer. The energy minima or the saddle points were confirmed by vibrational frequency calculations at the same level.

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(11) Hazinaga, S. *Approximate Atomic Wave Function*; University of Alberta: Edmonton, Alberta, 1971.

(12) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Steward, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A.; Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA 1984.