as DZP SCF results indicate. In agreement with some experimental evidence,[19] the present theoretical study suggests that aluminum has a stronger tendency to form "hyper"-valent structures than does gallium, and this may explain the difficulty in isolating dialane in spite its relatively high dimerization energy.

The energy differences between the cyclic and pentacoordinated trimers are surprisingly small. The DZP CISD predictions indicate that these two structures for trialane(9) may be nearly isoenergetic. The pentacoordinated triborane(9) is predicted to be only 3–4 kcal mol^{-1} (DZP CCSD) higher in energy than its well-known cyclic isomer. This new structure for triborane(9) may be involved in the early pyrolysis of diborane and could explain the dispute on the kinetics of this process.[8,9]

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Butadiene. 2. Examination of the Energetic Preference for Coplanarity of Double Bonds. Comparison of Butadiene, Acrolein, and Vinylamine

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Abstract: Experimental and theoretical studies show a 4–5 kcal/mol barrier to rotation for butadiene. What causes this barrier and what other features of butadiene change upon rotation? We have examined this question in terms of Hückel theory and Simpson's resonance force model. The latter predicts an important component from electron correlation which was not found. Hückel theory predicts significant double bond character for the central bond of planar butadiene. Butadiene and the related compounds acrolein and vinylamine were compared to the unconjugated model compounds, butane and the three butenes. Geometries, force constants, and integrated charge distributions of the conjugated compounds were found to be similar to their unconjugated 90° structures and to the model compounds. Integration of the charge density at the center of the single bond for the two π-MO's of butadiene relative to its 90° isomer did reveal significant extra π-electron density. However, the σ electrons were polarized in the opposite direction so as to minimize electron repulsion. The σ–π interaction explains why only small changes in bond lengths or force constants are seen. The electrostatic potential maps for the three compounds also were studied and were converted to their equivalent point charge models. Electrostatic potential differences among butadiene, acrolein, and vinylamine were found to be consistent with their reactivity differences.

1. Introduction

Butadiene has been of special interest to chemists for years. Despite the many studies, there remains the question of the origin of the preference for a planar conformation. This energetic preference is found from both thermochemical measurements and ab initio theory to be 3–5 kcal/mol.[1-3] Is this preference due to electron conjugation or to some other interactions such as a resonance force?[4] Simple Hückel theory successfully accounts for the energy preference and also predicts significant interaction across the C_2–C_3 bond of conjugated butadienes.[5] This results in double bond character imparted to the single bond and single bond character to the double bonds. We sought some evidence for this interaction. We have examined geometries looking at bond lengths as the torsional angle was changed. We have compared the butadiene rotamers to butane, the three butenes, acrolein, and vinylamine looking specifically for anomalous bond lengths. Acrolein was included as a case that may be expected to have more interaction across the 2,3 bond due to the contribution of the zwitterionic resonance structure caused by the polarization of the carbon oxygen bond. Vinylamine presumably would have a complementary zwitterionic resonance structure to that of acrolein, and also was examined. Ab initio calculations yielded force constants for the C—C and C═C bonds of the butadienes and butenes, acroleins, and vinylamines which were compared. The electron populations of the above compounds also were examined. The σ and π charge densities for planes perpendicular to the bond

Table I. Calculated Energies for Butadiene at Fixed Torsional Angles[a-c]

τ, deg	MP2/ 6-31G*	E_{rel}	MP3/ 6-311++G**	E_{rel}	ZPE	ΔH
0	−155.435 99	3.59	−155.561 27	3.59	51.53	3.42
37.73	−155.437 44	2.68	−155.563 17	2.40	51.66	2.36
45	−155.437 30	2.77	−155.563 12	2.43		
90.0	−155.432 66	5.68	−155.559 14	4.93		
101.64	−155.432 15	6.00	−155.558 76	5.16	51.31	4.78
135	−155.436 45	3.30	−155.562 61	2.75		
180	−155.441 71	0.00	−155.566 99	0.00	51.69	0.00

[a] The total energies are given in hartrees, and the relative energies and zero-point energies are given in kcal/mol. The MP3 energies were calculated at the MP2 geometries. [b] The gauche form had τ = 37.73° and the transition state had τ = 101.64°. [c] The MP2/6-31G* energies are slightly different than those reported in ref 2. They were obtained assuming the vinyl groups maintained planarity, whereas in the present calculations, this assumption was not made.

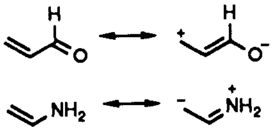

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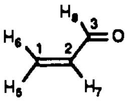
Table II. MP2/6-31G* Optimized and Experimental Geometries at Fixed Torsional Angles of Acrolein[a]

angle	C═C	CC	C═O	CH_6	CH_5	CH_7	CH_8	CCC	CCO	H_6CC	H_5CC	$H_7C{=}C$	H_8CC
180c	1.3406	1.4713	1.2256	1.0870	1.0843	1.0864	1.1105	120.54	124.00	121.00	122.30	122.46	114.98
180e	1.340	1.468	1.214	1.090	1.080	1.084	1.113	120.4	124.0	119.7	122.2	122.4	114.7
135c	1.3397	1.4790	1.2250	1.0870	1.0843	1.0868	1.1095	119.85	123.01	121.22	122.05	121.75	115.76
91.4c	1.3364	1.4937	1.2240	1.0857	1.0844	1.0887	1.1084	122.23	123.32	121.70	121.49	120.97	116.31[b]
45c	1.3393	1.4814	1.2258	1.0855	1.0844	1.0881	1.1082	120.67	124.00	120.44	122.02	121.31	115.52
0c	1.3400	1.4809	1.2267	1.0854	1.0842	1.0871	1.1072	120.77	123.90	119.88	122.15	121.67	115.90
0e	1.340	1.478	1.215	1.098	1.081	1.088	1.106	121.5	124.2	118.5	121.5	121.1	115.8



	torsional angle					
	0°	45°	90°	ts (91.42°)	135°	180°
MP2/6-31G* energy	−191.32624	−191.32231	−191.31558	−191.31556	−191.32330	−191.32858
rel energy (kcal/mol)	1.47	3.93	8.16	8.17	3.31	0.00
MP3/6-311++G**	−191.44652	−191.44428	−191.43887	−191.43884	−191.44545	−191.45009
rel energy (kcal/mol)	2.24	3.65	7.04	7.06	2.92	0.00
ZPE (kcal/mol)	37.54			37.03		37.53
Δ*H* (kcal/mol)	2.22			6.56		0.000

[a] The bond lengths are given in Å, and the bond angles in deg. The entries marked c are calculated values and those marked e are experimental. The total energies are given in hartrees.

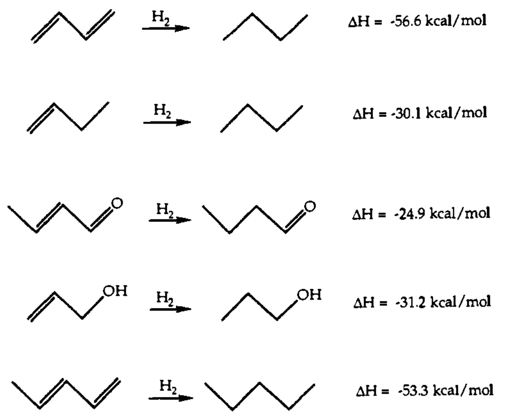


Figure 1. Enthalpies of hydrogenation of double bonds.

critical points of the C_2–C_3 bonds of butadiene and acrolein were integrated, shedding some insight into the above findings. The electrostatic potentials of both planar and rotated forms of all three molecules also were studied.

2. Thermochemistry

What is the energetic preference for coplanarity of the C_1–C_2 and C_3–C_4 groups in butadiene and acrolein? The thermochemical data given in Figure 1 show that the reduction of the double bond of 1-butene is 3.6 kcal/mol more exothermic than that for the first double bond of butadiene.[1] This is less than the rotational barrier of butadiene, which is estimated experimentally as 3.9, 4.3, or 4.9 kcal/mol[6] and theoretically (MP3/6-311++G**//MP2/6-31G* plus ZPE correction) as 4.78 kcal/mol (Table I).[2] This energy barrier is the sum of stabilization of the 0° form and destabilization of the 90° form of butadiene (with the reasonable assumption that all "conjugative" stabilization is lost at 90°). The destabilization energy at 90° would be expected to be minor as there are no obvious steric or electronic "problems" with the 90° structure. This is borne out as the rotational barrier is only about 1 kcal/mol higher than the thermodynamically estimated "conjugation" stabilization of 3.6 kcal/mol.

By combining the energy of hydrogenation of butadiene with the rotational barrier of butadiene and the rotational barrier of butane, we can derive the hydrogenation energy of 90° butadiene. This quantity minus the hydrogenation energy of butadiene is the stabilization energy of coplanar double bonds in butadiene. This scheme is shown graphically in Figure 2 and yields a stabilization energy of 3–4 kcal/mol with the uncertainty arising from the measurement of the rotational barrier.

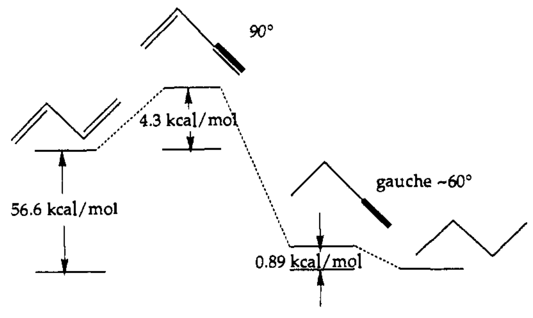
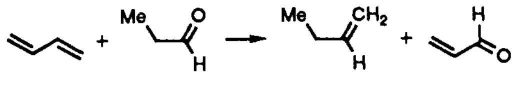


Figure 2. Steps in the hydrogenation of butadiene.

Acrolein has a similar energetic stabilization of 3 kcal/mol. The hydrogenation enthalpy of butenal is known, and by using the difference between the Δ*H*(hydrogenation) of 1,3-pentadiene and butadiene, the hydrogenation enthalpy of acrolein has been estimated to be −28.2 kcal/mol. When compared to the known hydrogenation energy of allyl alcohol,[7] the difference is 3.0 kcal/mol, which is only slightly smaller than that in butadiene. While 1-butene is a fair model for comparison of heats of hydrogenation with butadiene, allyl alcohol is somewhat less satisfactory. Ideally, the reduction of acrolein to propanal would be compared to the conversion of unconjugated acrolein to propanal. Allyl alcohol seemed a reasonable model and has a heat of hydrogenation near that of 1-butene. It can be seen that the stabilization energy of acrolein is essentially the same as that of butadiene.

A direct comparison with butadiene is available in considering the isodesmic reaction of *s-trans*-butadiene and eclipsed propanal going to *s-trans*-acrolein and *syn*-1-butene. This reaction is calculated at the 6-31G* level of theory to prefer the butadiene



side by 0.90 kcal/mol and found experimentally to be 1.7 kcal/mol, further corroborating the assumption above. The barrier to rotation for converting *s-trans*-acrolein to 90° acrolein is experi-

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Table III. Results of Geometry Optimizations

	trans-n-butane		1-butene		*cis*-2-butene		*trans*-2-butene	
	6-31G*	obs	6-31G*	obs	6-31G*	obs	6-31G*	obs
C_1C_2	1.5282	1.533	1.3191	1.342	1.5043	1.506	1.5031	1.508
C_2C_3	1.5297	1.533	1.5079	1.493	1.3222	1.346	1.3196	1.347
C_3C_4			1.5263	1.536				
CH_5	1.0857	1.108	1.0753	1.09	1.0820	1.095	1.0846	1.095
CH_6	1.0864	1.108	1.0756	1.09	1.0871	1.095	1.0872	1.095
CH_8	1.0881	1.108	1.0794	1.09	1.0790	1.09	1.0800	1.09
CH_9			1.0888	1.095				
CH_{10}			1.085	1.095				
CH_{11}			1.0852	1.095				
$C_1C_2C_3$	113.08	112.4	127.21	125.4	128.35	125.4	125.21	123.8
$C_2C_3C_4$			115.86	112.1				
$H_5C_1C_2$	111.30	110.5	122.74	122.46	113.05	109.5	111.44	109.6
$H_6C_1C_2$	111.14	110.5	121.11	121.68	110.48	109.5	111.05	109.5
$H_8C_2C_3$	109.25	110.5	118.28	117.1	117.15	117.39	118.96	117.39
$H_9C_3C_2$			108.16	110.3				
$H_{10}C_4C_3$			110.37	110.3				
$H_{11}C_4C_3$			111.33	110.3				
$H_6C_1C_2C_3$	59.93	60.0	123.18	119.9				
$H_8C_2C_3C_4$	57.91	60.0	60.31	60.0	120.95	120.0	120.54	120.0

mentally measured at 4.0 or 5.0 kcal/mol[8] and computationally at 6.56 kcal/mol (Table II).[9] The rotation barrier is thus about 1 kcal/mol higher than the thermodynamically estimated stabilization energy of the planar rotamer. This is very similar to butadiene.

3. Theoretical Studies: Bond Lengths and Force Constants

Calculations were performed with a Trace 7 minisupercomputer or Microvax GPX workstation and the Gaussian 86 package of programs.[10] All computations were done at the 6-31G* level of theory with full optimizations at that level,[11] unless otherwise noted.

Having established that some stabilization energy is present in the planar forms of butadiene and acrolein, we sought to explain this stabilization. Two theories have previously been used. One, Hückel theory, predicts an energy stabilization for butadiene of 7 kcal/mol, which is remarkably close to the 3–4 kcal/mol found experimentally.[5] Moreover, Hückel theory predicts that the terminal double bonds of butadiene will have a bond order of 1.9 and the central bond of 1.4.[13] The second less familiar theory is due to Simpson, who proposed a resonance force model.[4] Briefly, the temporary polarization of one double bond of butadiene polarizes the other double bond. This interaction becomes stronger as the double bonds come closer to planarity. The two polarized bonds interact favorably, but no bond order change is predicted for the double and single bonds. This is an internal dispersive interaction which should not be found at the Hartree–Fock level, but would be found when correction for electron correlation is made.

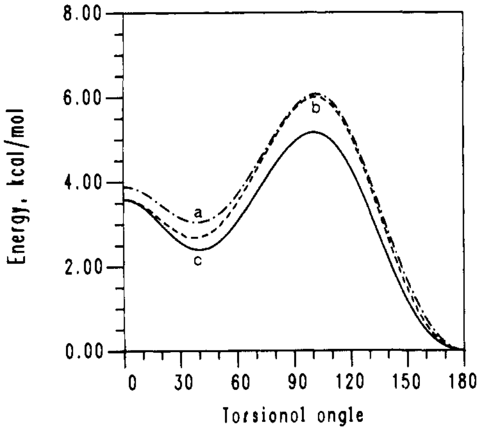

Figure 3. Calculated energy for butadiene as a function of the C–C–C–C torsional angle. The curves are (a) 6-31G*, (b) MP2/6-31G*, and (c) MP3/6-311++G**//MP2/6-31G*.

Computationally, we have obtained the fully optimized geometries of butadienes fixed at given torsional angles in order to analyze the above theories. Both HF/6-31G* and MP2/6-13G* optimizations were performed.[2] Plots of energy versus torsional angle (Figure 3) were remarkably similar for both levels of theory. As Simpson's model would not be correctly computed with Hartree–Fock (HF) theory, and only would be included in a post-HF calculation, it is clear that his model is disproved by the above observations. This leaves us with Hückel theory.

Hückel theory predicts that butadiene will have long double bonds and short single bonds. Yet upon rotation butadiene was found to have double bond changes of only 0.004 Å and single bond changes of 0.02 Å.[2] The same differences between the 180° and 90° conformers of acrolein were found (Table II). How much of the 3 kcal/mol of stabilization energy is reflected in the shorter C–C bond length of the planar rotamer? Calculations for *trans*-butadiene with the C–C cental bond lengthened 0.03 Å show only a 0.36 kcal/mol energy increase or 12% of the total stabilization energy. Thus the minor bond length changes of butadiene and acrolein upon rotation do not account for the energetic stabilization of the planar forms.

However, the double bond and single bond lengths of the dienes are not the same as those of the model compounds, 1-butene, the 2-butenes, and *n*-butane.[12] The calculated structures are given in Table III and the conformations are shown in Figure 4. While the double bond lengths are remarkably similar, the single bond lengths are quite different. There also are significant single bond length differences between acrolein and butadiene. One notes a steady progression in single bond length from 1.53 to 1.50 to 1.47

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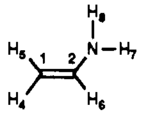
Table IV. 6-31G* Force Constants for C=C and C—C Stretching Modes of Butanes and Butenes[a,b]

compound	rotamer	r(C=C)	f(C=C)	bond order	ρ at c.p.	r(C—C)	f(C—C)	bond order	ρ at c.p.
butadiene	cis	1.3223	11.19	1.95	0.3611	1.4798	5.74	1.03	0.2791
	gauche	1.3214	11.30	1.97	0.3615	1.4782	5.71	1.03	0.2796
	90°	1.3186	11.50	2.00	0.3629	1.4893	5.56	1.00	0.2747
	trans	1.3226	11.26	1.96	0.3621	1.4676	5.85	1.05	0.2850
1-butene		1.3191	11.44	1.99	0.3626	1.5079	5.25	1.00	0.2651
2-butene	cis	1.3222	11.41	1.98	0.3606	1.5043	5.28	1.01	0.2644
	trans	1.3196	11.43	1.99	0.3635	1.5031	5.34	1.01	0.2654
butane	trans					1.5297	4.90	1.00	0.2561
acrolein	cis	1.3212	11.26	1.96	0.3632	1.4861	5.42	0.98	0.2833
	90°	1.3165	11.58	2.01	0.3620	1.4986	5.11	0.92	0.2792
	trans	1.3211	11.32	1.97	0.3638	1.4783	5.48	0.99	0.2879
vinylamine	0°	1.3251	10.99	1.91	0.3564				
	eq	1.3218	11.15	1.94	0.3601				
	90°	1.3175	11.48	2.00	0.3692				

[a] Bond lengths in Å, force constants in mdyn/Å, and ρ in e/bohr^3. [b] In the calculation of bond orders, the standard values of force constants were taken as 4.90 for sp^3–sp^3, 5.25 for sp^3–sp^2, 5.56 for sp^2–sp^2, and 11.5 for C=C.

Table V. HF6-31G* Optimized Geometries at Fixed Torsional Angles of Vinylamine (Planar NH_2)[a]

angle	C=C	CN	CH_4	CH_5	CH_6	NH_7	NH_8	CCN	H_4CC	H_5CC	H_6CC	H_7NC	H_8NC
0	1.3251	1.3714	1.0727	1.0766	1.0766	0.9900	0.9923	127.12	120.36	122.19	119.73	121.25	121.10
22.5	1.3240	1.3763	1.0732	1.0764	1.0767	0.9904	0.9919	126.76	120.35	122.16	119.58	121.10	121.22
45	1.3213	1.3892	1.0742	1.0760	1.0792	0.9910	0.9910	125.67	120.58	121.90	119.36	120.92	121.36
67.5	1.3188	1.4025	1.0753	1.0756	1.0809	0.9913	0.9907	124.49	120.85	121.60	119.14	120.95	121.32
90	1.3180	1.4083	1.0757	1.0755	1.0816	0.9911	0.9911	123.98	121.04	121.43	119.05	121.11	121.11
eq	1.3218	1.3929	1.0732	1.0769	1.0767	0.9982	0.9973	126.74	120.60	122.11	119.98	114.27	114.14



	torsional angle					
	0°	22.5°	45°	67.5°	90°	eq
energy (hartrees)	−133.05920	−133.05706	−133.05200	−133.04717	−133.04525	−133.06170
rel energy (kcal/mol)	1.57	2.91	6.09	9.12	10.32	0.0

[a] The amino group was held planar in all cases except the last (eq) which is the minimum energy geometry with a nonplanar amino group.

Å on going from butane to butene to butadiene. This bond length change can be accounted for with a simple hybridization model.[13] The sp^2 bonds have more s character and are more electronegative than the sp^3 bonds. This results in a 0.03-Å shortening on going from butane to butene (note that 1-butene and the 2-butenes have the same sp^2–sp^3 C–C single bond length). Thus we would expect butadiene to have a still shorter single C–C bond, as is observed. The change in C–C bond length on rotation is relatively small.

Thus it is seen that the coplanarity of double bonds results in an energy stabilization that is not fully reflected in any bond length change. Perhaps the double bonds in butadiene are weaker and the single bonds stronger than in the model compounds with similar bond lengths. This factor would be revealed by looking at the C—C and C=C stretching force constants for these molecules.

Ab initio calculations of vibrational spectra provide force constants for internal coordinates directly. The single and double bond stretching constants for several butadienes, acroleins, vinylamines, and the model C_4 hydrocarbons obtained with the 6-13G* basis set are shown in Table IV. The geometrical parameters for vinylamine are given in Table V. It is known that the force constants thus obtained are about 20% too large, but the scaling factors have been found to be essentially the same for closely related systems.[14] Thus, errors should cancel allowing the calculated force constants to be compared in a useful fashion.

Several points are of interest. The double bonds of the conjugated molecules are weaker than the unconjugated and model compounds, consistent with Hückel theory. However, the magnitude of this change is quite small, only 1–2%, and near the error limits of the computational approach. Once again the C=C

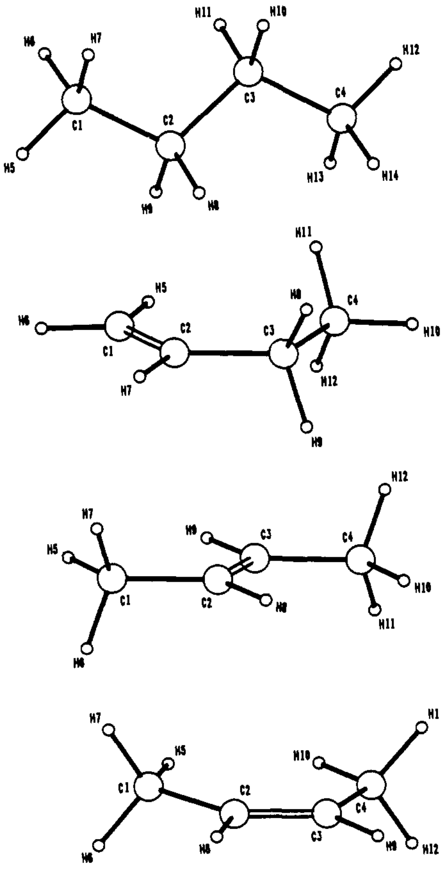


Figure 4. Conformers of the C_4 hydrocarbons.

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(14) Cf.: Wiberg, K. B.; Waddell, S. T.; Rosenberg, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 2184. Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J.; Vorgha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7037.

Table VI. Electron Populations for Butadienes with the 6-31G** Basis

τ, deg		C_1	C_2	H_5	H_6	H_7	Σ_{CH_2}	Σ_{CH}	Σ_{all}
0.0		5.924	5.946	1.045	1.037	1.050	8.006	6.996	30.004
38.1		5.917	5.958	1.038	1.039	1.047	7.994	7.005	29.998
45.0		5.916	5.962	1.036	1.040	1.046	7.992	7.008	30.000
90.0		5.913	5.970	1.037	1.041	1.039	7.991	7.009	30.000
135.0		5.922	5.957	1.042	1.039	1.040	8.003	6.997	30.000
180.0		5.927	5.946	1.043	1.037	1.045	8.007	6.991	29.996
				π Electron Populations					
180	ϕ_{14}	0.353	0.608	0.011	0.010	0.018	0.373	0.626	1.998
	ϕ_{15}	0.604	0.342	0.020	0.021	0.011	0.646	0.353	1.998
sum		0.957	0.950	0.031	0.031	0.029	1.019	0.979	3.996
90	ϕ_{14}	0.484	0.440	0.017	0.017	0.040	0.518	0.481	1.998
	ϕ_{15}	0.476	0.451	0.016	0.017	0.039	0.510	0.490	2.000
sum		0.960	0.891	0.033	0.034	0.079	1.028	0.971	3.998
0	ϕ_{14}	0.356	0.605	0.011	0.010	0.017	0.377	0.623	2.000
	ϕ_{15}	0.594	0.352	0.019	0.021	0.014	0.634	0.366	2.000
sum		0.950	0.957	0.030	0.031	0.031	1.011	0.989	4.000

Table VII. Electron Populations for Butane and Butenes, 6-31G**

molecule	C_1	C_2	H_5	H_6	H_8	Σ_{CH_3}	$\Sigma_{C_2H's}$	Σ_{all}
n-butane	5.775	5.790	1.079	1.082	1.095	9.018	7.980	33.996
cis-2-butene	5.763	5.974	1.069	1.065	1.063	8.962	7.037	31.998
trans-2-butene	5.758	5.974	1.068	1.067	1.065	8.960	7.039	31.998

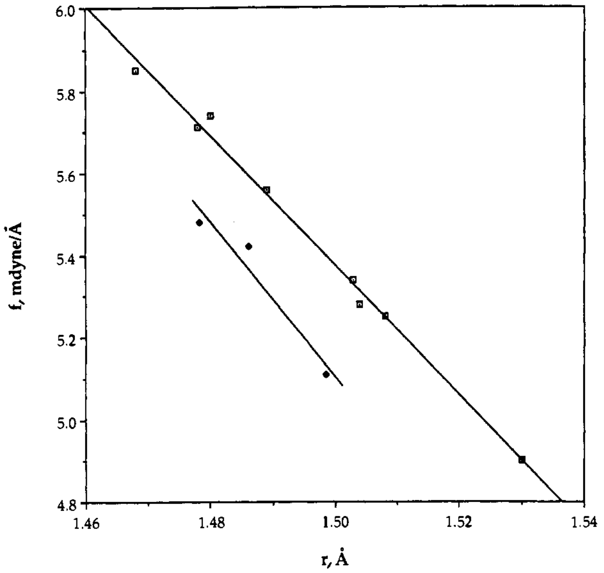

Figure 5. Relationship between the C–C single bond force constants and the C–C bond lengths. The full line gives the correlation for butane and the C_4 alkenes, and the short line gives the correlation for the cis, trans, and saddle-point conformers of acrolein.

double bond of acrolein in both planar and perpendicular geometries is remarkably similar to that of butadiene. Single bond force constant changes are more substantial. They also are closely related to single bond lengths, as is shown in Figure 5. The shorter bonds have the higher force constants, and this leads to an economy in explaining the force constants. The hybridization model works for all comparisons, with the only significant change being the slight lengthening and hence weakening of the C–C single bonds in the nonconjugated forms. This is an effect of only 3–4% and is much less than the 40+% change predicted for Hückel theory.

Assuming a linear progression of force constants between single and double bonds, the bond orders for the various single and double bonds were estimated and are given in Table IV. Here, the bond order is given by 2.0 − (standard double bond force constant − force constant)/(standard double bond force constant − standard single bond force constant). This model is only an approximation. Nevertheless, some trends are apparent: the bond orders are shifted about 3–5% toward that expected from the appropriate resonance form. This effect is again much smaller than that predicted by Hückel theory.

4. Charge Densities and Electron Populations

The next property of the conjugated systems we sought to investigate is the charge density distribution. Hückel theory predicts a bond order of 1.4 for the C_2–C_3 bond of butadiene. Do we expect to see a theoretical electronic charge redistribution? The resonance structures for acrolein and vinylamine suggest a ground state charge transfer which would be eliminated by a 90° rotation about the central bond. Will the expected change in charge distribution be observed?

Bader has developed a unique and quantum mechanically rigorous method for defining an atom.[15] Briefly, the bond critical

Table VIII. Electron Populations for Acroleins, 6-31G**[a]

τ, deg		O	C_1	C_2	C_3	H_5	H_6	H_7	H_8	Σ_{CH_2}	Σ_{CH}	Σ_{all}
180		9.321	5.948	5.951	4.700	1.022	1.009	1.002	1.049	7.979	6.953	30.002
135		9.316	5.924	5.982	4.696	1.027	1.014	1.004	1.040	7.965	6.986	30.003
90		9.310	5.888	6.010	4.694	1.025	1.021	1.013	1.037	7.934	7.023	29.998
45		9.318	5.903	5.992	4.701	0.999	1.019	1.027	1.045	7.921	7.019	30.004
0		9.327	5.922	5.972	4.700	0.976	1.016	1.037	1.048	7.914	7.009	29.998
						π Electron Populations						
180	ϕ_{13}	1.324	0.056	0.165	0.434	0.002	0.001	0.004	0.015	0.059	0.169	
	ϕ_{15}	0.270	0.830	0.797	0.026	0.026	0.026	0.024	0.001	0.881	0.821	
sum		1.594	0.886	0.962	0.461	0.027	0.027	0.028	0.016	0.940	0.990	
90	ϕ_{13}	1.357	0.073	0.116	0.283	0.035	0.001	0.123	0.013	0.109	0.117	
	ϕ_{14}	1.121	0.038	0.256	0.198	0.021	0.045	0.050	0.271	0.104	0.306	
	ϕ_{15}	0.037	0.911	0.909	0.030	0.028	0.028	0.028	0.027	0.968	0.937	
0	ϕ_{13}	1.343	0.052	0.157	0.427	0.002	0.001	0.003	0.015	0.055	0.160	
	ϕ_{15}	0.261	0.792	0.847	0.026	0.022	0.024	0.028	0.001	0.838	0.875	
sum		1.604	0.844	1.003	0.451	0.024	0.026	0.032	0.016	0.892	1.035	

[a] See Table II for atom labels.

Table IX. Electron Populations for Vinylamines, 6-31G**

τ, deg		N	C_1	C_2	H_4	H_5	H_6	H_7	H_8	Σ_{CH_2}	Σ_{CH}	Σ_{all}
0.0		8.437	5.820	5.470	1.050	1.066	1.038	0.558	0.560	7.936	6.508	23.999
22.5		8.435	5.846	5.446	1.049	1.061	1.041	0.561	0.559	7.956	6.487	23.998
45.0		8.428	5.884	5.415	1.048	1.050	1.047	0.566	0.559	7.982	6.462	23.997
67.5		8.417	5.910	5.397	1.046	1.038	1.055	0.569	0.563	7.994	6.452	23.995
90.0		8.411	5.925	5.390	1.045	1.033	1.059	0.568	0.568	8.003	6.449	23.999
eq		8.330	5.849	5.487	1.044	1.060	1.038	0.596	0.596	7.947	6.525	23.994
					π Electron Populations							
0	ϕ_{14}	1.314	0.176	0.463	0.004	0.005	0.014	0.011	0.011	0.186	0.477	
	ϕ_{15}	0.588	0.903	0.412	0.034	0.033	0.013	0.008	0.008	0.971	0.425	
sum		1.902	1.079	0.875	0.039	0.038	0.027	0.019	0.019	1.156	0.902	
90	ϕ_{14}	1.652	0.074	0.082	0.011	0.007	0.135	0.020	0.020	0.092	0.216	
	ϕ_{15}	0.093	0.938	0.824	0.031	0.029	0.029	0.028	0.028	0.998	0.853	
sum		1.745	1.012	0.905	0.042	0.036	0.164	0.048	0.048	1.090	1.069	

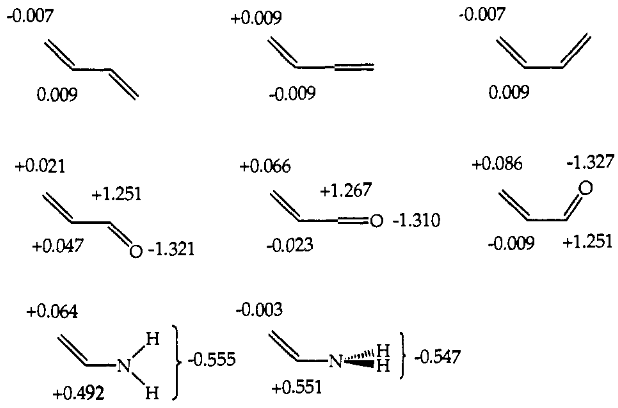

Figure 6. Group charges derived from electron populations.

point along each bond (i.e., the point having the minimum charge density along the bond, but a maximum normal to the bond) is located. Starting at this point, rays are developed corresponding to paths along which the charge density decreases most rapidly. The set of these rays from a given critical point defines a surface, and the set of surfaces (one from each critical point) will divide space into a set of atomic domains. Numerical integration of the charge density within a domain gives the electron population for that atom. The PROAIMS package[16] was used to integrate these atoms, and the results are summarized in Tables VI–IX. The atom charges derived from the populations are shown in Figure 6.

The integrated atomic populations for butadiene are essentially constant with respect to torsional rotation. Moreover, the terminal CH_2 has 8.007 electrons which is close to the expected 6 + 1 + 1 = 8.000 e, while the middle CH has 6.991 e as compared to the expected 6 + 1 = 7.000 e. The vinyl CH_2 in acrolein would be expected to show significant charge depletion in a Hückel-like system. Instead the population of the vinyl group in acrolein is close to that of butadiene with some small changes upon rotation. The small change in population on rotation results from a coulombic interaction between the carbonyl group and the double bond in *cis*-acrolein. The large C═O bond dipole will cause a charge shift in the C═C group of the cis form leading to an induced dipole with the opposite sense to the C═O dipole. In this way, the electron population at the terminal methylene group of the cis form will be reduced. In vinylamine the population at the CH_2 changes smoothly from 7.936 e in the 0° form to 8.003 e in the 90° conformer. These numbers are quite similar to those for both butadiene and acrolein. Thus, the atomic populations indicate that little, if any, net ground state charge transfer occurs in either acrolein or vinylamine.

One also can examine the π atomic populations using this analysis. While the separation between σ and π in the 90° forms is not a strict one, some semiquantitative results are available. For butadiene the population at the terminal CH_2 increases by 0.015 e on going from the 180° to the 90° conformer and decreases 0.016 e upon rotation to the 0° form. Both changes are negligible. For acrolein the π population at the methylene group decreases by 0.05 e on going from the 180° to the 0° form. This change is due to the polarizing effect of the C═O dipole on the π system of the C═C bond in the 0° conformer. The populations for the 90° form are more difficult to interpret. However, since ϕ_{15} (largely the terminal C═C) has a larger population for the CH_2 group than does the sum of the populations for this group in either of the planar forms, there must be some π-shift due to the interaction with the carbonyl group in the planar forms.

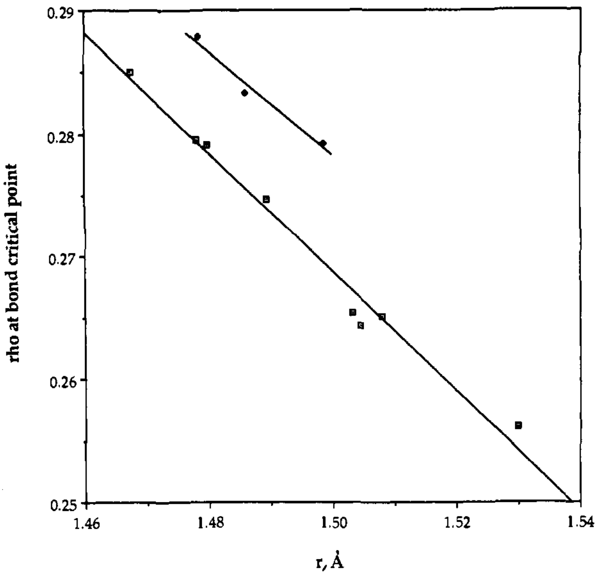

Figure 7. Relationship between the value of ρ (e/bohr^3) at the bond critical point and the C–C bond length. The full line gives the correlation for butane and the C_4 alkenes, and the short line gives the correlation for the cis, trans, and saddle-point conformers of acrolein.

Another quantity obtainable from the analysis is the value of ρ at the bond critical point described above. Perhaps the value of ρ is a sensitive monitor of the charge buildup or depletion in a bond. A plot of ρ versus bond length (Figure 7) shows that for all compounds examined ρ varies linearly with the inverse of the bond length for single bonds as would be expected in the absence of other factors. It is highly scattered for double bonds. However, the range of both double bond lengths and values of ρ are so small that no firm conclusion can be drawn. Hence, ρ values are consistent with all other indicators that the Hückel predictions of considerable changes in the single and double bond properties for butadiene relative to "normal" single and double bonds are not realized.

While Hückel theory predicts butadiene, acrolein, and vinylamine to be more stable when conjugated, it also predicts significant bond length and force constant changes which are clearly not seen. To seek the origin of the 3.5-kcal/mol stabilization of

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(15) (a) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9. (b) Srebrenik, S.; Bader, R. F. W. *J. Chem. Phys.* **1974**, *61*, 2536.

(16) Biegler-Koenig, F. N.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317.

Table X. Electron Populations for Planes Passing through Bond Critical Points

rotamer	geom	bond	population π	population σ	population total
		Butadiene			
trans	equil	C_2–C_3	0.201	1.151	1.352
90°	equil	C_2–C_3	0.111	1.185	1.296
cis	equil	C_2–C_3	0.187	1.104	1.291
trans	90°	C_2–C_3	0.192	1.116	1.308
cis	90°	C_2–C_3	0.183	1.089	1.272
trans	equil	C_1–C_2	0.386	1.266	1.652
90°	equil	C_1–C_2	0.428	1.229	1.656
		Acrolein			
trans	equil	C_2–C_3	0.173	1.126	1.299
90°	equil	C_2–C_3	0.089	1.142	1.231
cis	equil	C_2–C_3	0.171	1.107	1.278
trans	90°	C_2–C_3	0.165	1.094	1.259
cis	90°	C_2–C_3	0.167	1.090	1.256

planar butadiene, we decided to look at the charge distribution directly. Numerical grids of ρ in a plane perpendicular to the center of the vector connecting two atoms were generated directly from the ab initio wave function. All the points in these grids were summed to give the electron population for a given set of MO's along a given bond.

For butadiene the π MO's are clearly identified as the two highest occupied MO's. Summing the charge density in a plane perpendicular to the C–C bond at its mid-point should indicate how much π density has accumulated in the C–C bond. By using this approach a population of 0.201 e/Bohr is found for *s-trans*-butadiene and a population of 0.111 e/Bohr is found for 90° butadiene (Table X). This comparison is biased as the C–C length is shorter in the s-trans compound. Thus, we have repeated the calculation with *s-trans*-butadiene frozen at the 90° butadiene C–C bond lengths. Here, 0.192 e/Bohr is found at the minimum along the C–C bond. From these numbers it is clear that there is significantly less π electron density in the C–C bond of 90° butadiene versus the planar rotamer. Interestingly about 10% of the π electron density difference is reflected purely in the shorter C–C bond length of the planar rotamer. Integrating normal to the C=C bonds for s-trans gives a density at the minimum along the bond of 0.386 e/Bohr. This comparison shows that while most of the π electron density is in the C=C bond, a significant density is accumulated in the center of the C–C bond as predicted by Hückel theory. The comparison between 90° butadiene and *s-trans*-butadiene is unavoidably skewed, as the σ,π separation in 90° butadiene is not clean. Nevertheless, the MO coefficients for the σ orbitals in the two highest MO's for 90° butadiene are small, and we feel the results have some semiquantitative value.

The simple interpretation of this result is that the overlap of the p orbitals at C_2 and C_3 in the planar form leads to an increase in π-charge density over that in the 90° form. However, the data in Table X show that the total density at the center of the C–C bond is essentially the same for the trans and 90° forms, and that the change in π density is compensated by an opposing change in σ density. The compensation presumably arises from the need to minimize electron repulsion. Since there is little net change in charge density, it is not surprising that the properties change so little on rotation.

For acrolein, the above analysis is complicated by the presence of the oxygen lone pairs, which in the 90° rotamer mix in with the C=C π electrons. This results in generally lower densities in acrolein than in butadiene. Nevertheless, the results are qualitatively similar to those of butadiene. The s-trans rotamer has 0.173 e/Bohr for the π electrons in the central C–C bond slice which lessens slightly to 0.165 e/Bohr when the geometry is changed to mirror the 90° form. The latter has 0.089 e/Bohr in the central slice. Thus in both acrolein and butadiene the lengthening of the C–C bond decreases the density about 0.01 e/Bohr but rotation to the 90° rotamer results in a loss of 0.07 e/Bohr. We are thus led to conclude that the reason for the stabilization of the planar dienes over their 90° counterparts is due to delocalization of the π electrons but that the resulting geometry and force constant changes are much smaller than one would expect from Hückel-type arguments because of the σ polarization.

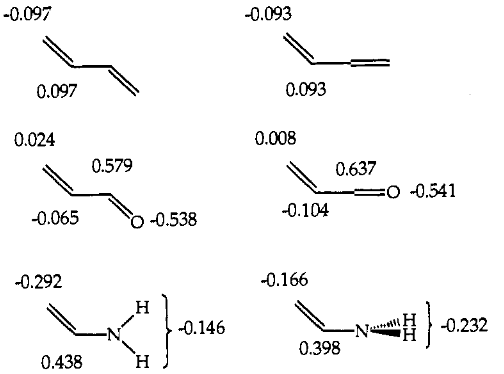

Figure 8. Effective charges derived from the electrostatic potentials.

The calculations are, of course, for the gas phase, and one might expect some increase in polarization on going to a solvent of high dielectric constant. This has been explored by Katritzky and Karelson[17] using reaction field theory with semiempirical MO calculations and by us using ab initio MO theory.[18] In both cases some increase in calculated dipole moment was found on going from the gas phase to solution.

5. Electrostatic Potentials

The reactivity of butadiene, acrolein, and vinylamine toward electrophiles and nucleophiles varies greatly, and in a sense expected from the dipolar resonance structures which are commonly written. However, this is not reflected in the electron populations derived from the molecular wave functions. Is it possible that there are important details of the charge distribution which are lost when it is averaged over atomic domains?

The electrostatic potential is another well-defined quantity which may be obtained from the molecular wave function. It is the energy of a positive test charge at a given location, and it can be calculated for a variety of locations leading to a grid of points. It has been found possible to reproduce the three-dimensional electrostatic potential maps via a set of effective point charges. The CHELP procedure[19] was used as modified to give rotational invariance[20] and led to the charges summarized in Table XI.

An examination of these charges (Figure 8) led to several interesting observations. Rotation of butadiene or acrolein resulted in only small changes of the CHELP charges at the CH_2 terminus, in agreement with Bader atomic integrations. However, a larger change was found with vinylamine and this change was in the direction expected from the zwitterionic resonance form of vinylamine. As electrostatic potentials are affected by both local and nearby charges it is not surprising that vinylamine exhibits larger changes in electrostatic potential at the CH_2 than acrolein as the electronegative atom and its lone pairs are closer. The differences in the CHELP charges at the CH_2 termini among butadiene, acrolein, and vinylamine reveal that the changes are consistent with a nucleophilic carbon of vinylamine, a mildly electrophilic center at the terminal carbon of acrolein, and a strongly electrophilic center at the carbonyl carbon of acrolein.

While the CHELP charges recover the familiar reactivity behavior of the title compounds, it might seem somewhat surprising that the CHELP charges differ so much from the charges derived by integrating the charge densities (Figure 6). However, it is important to recognize that the atoms defined in the theory of atoms in molecules are nonspherical whereas the CHELP atoms are spherically symmetric. Since the atoms in the former theory do not have the center of charge density coincident with the nuclei, a full description of the atoms requires a series expansion including

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(17) Katritzky, A.; Karelson, M. *Tetrahedron Lett.* **1990**, *31*, 2987.

(18) Wiberg, K. B.; Wong, M. W.; Frisch, M. To be published.

(19) Chirlian, L. E.; Francl, M. M. *J. Comput. Chem.* **1987**, *8*, 894.

(20) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.

Table XI. Effective Charges Derived from Electrostatic Potentials

	charge													
	C_1	C_2	C_3	N	O	H_4	H_5	H_6	H_7	H_8	Σ_{CH_2}	Σ_{CH}	$\Sigma_{CH'}$	Σ_{NH_2}
							Butadiene							
trans	−0.440	−0.003					0.165	0.178	0.100		−0.097	0.097		
90°	−0.415	0.027					0.157	0.165	0.066		−0.093	0.093		
							Acrolein							
trans	−0.310	−0.214	0.609		−0.538		0.160	0.174	0.149	−0.030	0.024	−0.065	0.579	
90°	−0.320	−0.246	0.710		−0.540		0.164	0.164	0.142	−0.073	0.008	−0.104	0.637	
							Vinylamine							
trans	−0.709	−0.346		−0.950		0.178	0.239	0.092	0.397	0.411	−0.292	0.438		−0.142
90°	−0.525	0.400		−0.983		0.159	0.200	−0.002	0.378	0.377	−0.166	0.398		−0.228

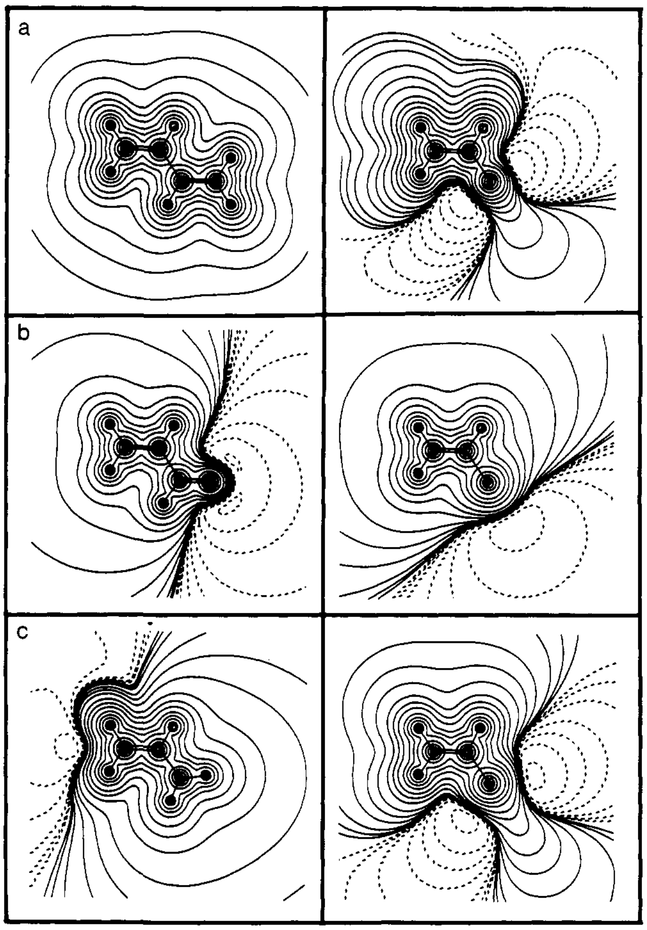

Figure 9. Electrostatic potential maps for the molecular plane of the vinyl groups. The planar forms are given at the left, and the 90° rotated forms are given at the right. The compounds are (a) butadiene, (b) acrolein, and (c) vinylamine.

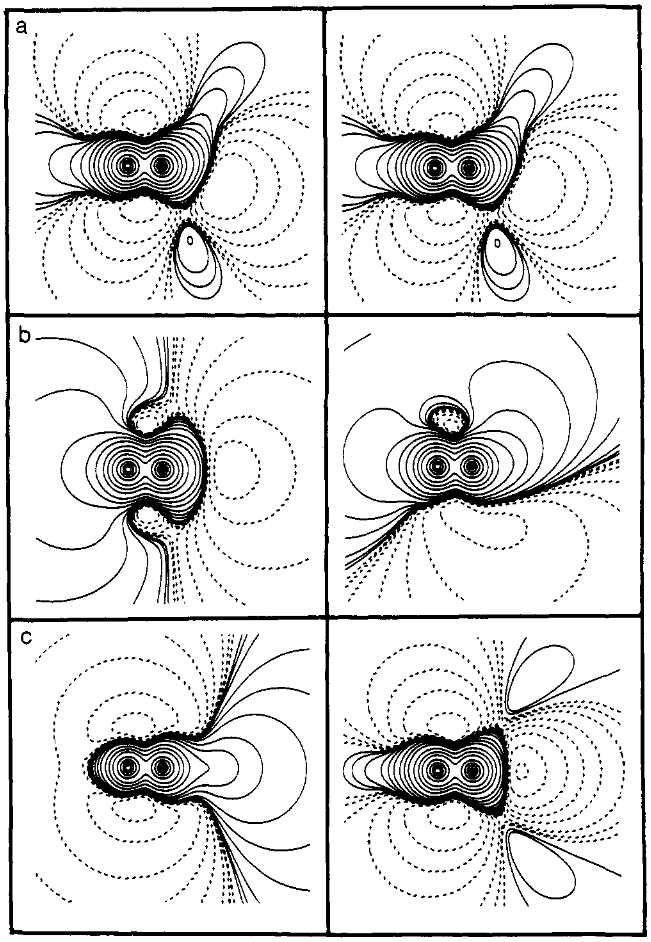

Figure 10. Electrostatic potential maps for a plane containing the π electrons of the vinyl groups. The arrangement is the same as for Figure 9.

dipolar, quadrupolar, and possibly higher terms. The connection between the physical atoms derived from the theory and the nonphysical atoms defined in the CHELP procedure is found when the electrostatic potential map is derived from both descriptions. We have found[21] that both the CHELP charges and the series expansion lead to the same electrostatic potential maps.

A more complete description of electrostatic potential than that available from CHELP may be obtained. An ab initio wave function was used to calculate the electrostatic potential on a point by point basis of a selected plane of the molecule of interest. Figure 9 shows the 6-31G* analytically derived two dimensional electrostatic potential maps for the molecular planes of the $H_2C{=}C$ groups of planar and 90° butadiene, acrolein, and vinylamine. Figure 10 shows the corresponding maps for planes containing the π electrons of the vinyl groups. Regions of negative potential are signified by dotted lines and are regions vulnerable to electrophilic attack. The solid lines are regions of positive potential and are regions susceptible to nucleophiles. One should also note that only regions outside the van der Waals' surfaces have any significance in this analysis.

In the planar version of butadiene (Figure 9) the potential is positive everywhere. When rotated 90°, very little change is seen in the potential near the $H_2C{=}C$ group. Acrolein has a potential map similar to that for butadiene, but the potential decays more slowly with distance from the nuclei. Upon rotation, the vinyl group looks more like butadiene. The interesting case is vinylamine. Regions of negative potential exist outside the CH_2 group suggesting an area of electrophilic attack, consistent with its chemical behavior. Interestingly, when the molecule is rotated the CH_2 region has no negative potential and looks like butadiene.

The π plane exhibits greater differences among the molecules. With butadiene, areas of negative potential appear symmetrically above and below the center of the C=C bond. This is just the region in which one would expect electrophilic reactions to occur. Upon rotation the map is changed only slightly. Acrolein, however,

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(21) Wiberg, K. B.; Breneman, C. M. To be published.

has only very small pockets of negative density above and below the π plane, suggesting that the vinyl group of acrolein is not at all susceptible to electrophilic assault. Moreover, significant positive potential exists well out along the C=C axis suggesting increased susceptibility toward nucleophilic attack. Upon rotation of the carbonyl group, the region above the C=C group is now similar to butadiene, while that region below the C=C group (in the direction of the carbonyl rotation) looks like that of planar acrolein. Vinylamine resembles butadiene above and below the plane but has negative density out along the C=C axis. Again this suggests that electrophilic addition reactions can occur along this axis. When the NH_2 group is rotated out of plane, however, the vinyl group is quite similar to butadiene. We thus see that analytic electrostatic potential maps can recover the chemical reactivity data about a molecule that is often lost in other methods of analyzing charge density distribution.

6. Conclusions

An analysis of the properties of cis, trans, and 90° rotated butadienes showed that the properties of the bonds are not much affected by rotation. However, the π-electron population at the center of the C_2–C_3 bond in butadiene is considerably greater in the trans form than in the 90° rotated form. This is compensated by the opposing change in σ electron population leading to little net change. Thus, the description of the π-electron system which arises from the simple Hückel approach is essentially correct, but a description of the molecule requires that both σ and π electrons be considered.

The vinyl group of acrolein was found to be similar to that of butadiene. Some differences were found with vinylamine, but here the main difference is found with the electrostatic potential which correctly indicates its reactivity toward electrophiles.

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Registry No. Butadiene, 106-99-0; acrolein, 107-02-8; 1-butene, 106-98-9; *trans-n*-butane, 106-97-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; vinylamine, 593-67-9.

Explanation of the Unexpected Differences in the Ground States of Dimethyl- and Dichlorobis(1,2-bis(dimethylphosphino)ethane)titanium

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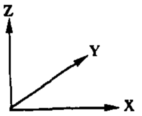
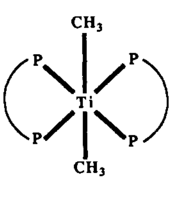
Abstract: Experimentally, $Ti(CH_3)_2(dmpe)_2$ has a *diamagnetic* singlet ground state while $TiCl_2(dmpe)_2$ has a *paramagnetic* triplet ground state. However, the stronger π donor, Cl, is expected to cause a larger splitting of the t_{2g}-like orbitals. Hence, if the ground states are different one would expect $TiCl_2(dmpe)_2$ to be diamagnetic and $Ti(CH_3)_2(dmpe)_2$ to be paramagnetic. In agreement with this simple reasoning, approximate molecular orbital calculations also predict a result contrary to experiment. Ab initio calculations with reasonable basis sets are required to produce qualitative agreement with the experimental results, while quantitative agreement requires significant correlation energy. Results reported here include single-determinant, generalized-valence-bond, complete-active-space, and direct configuration-interaction calculations in several basis sets on the title compounds and several model compounds. The explanation of the differences in states lies in the electronegativity difference between Cl and CH_3. The more electronegative Cl withdraws enough charge from the Ti to contract the d orbital sufficiently to cause the increased d–d electron repulsions in the Cl complex to outweigh the orbital splitting.

Introduction

A recent X-ray diffraction study on $Ti(CH_3)_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane][1] found it to be isostructural with $TiCl_2(dmpe)_2$.[2] Both compounds are pseudooctahedral with chelating phosphines in a rectangular-equatorial plane and Cl's or CH_3's in the axial positions. The coordination spheres for $Ti(CH_3)_2(dmpe)_2$ and $TiCl_2(dmpe)_2$ are shown in **1** and **2**, respectively. Surprisingly, Girolami and co-workers found $Ti(CH_3)_2(dmpe)_2$[1] to be *diamagnetic*, a singlet ground state, while $TiCl_2(dmpe)_2$[2] was known to be *paramagnetic*, a triplet ground state.





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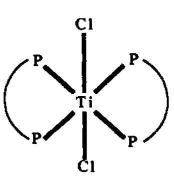

2

In a pseudooctahedral system the metal 3d orbitals divide into a low-lying t_{2g}-like set and a high-lying e_g-like set. Since $Ti(CH_3)_2(dmpe)_2$ and $TiCl_2(dmpe)_2$ are d^2 metals, the electrons of interest will occupy the t_{2g}-like orbitals. The energy of the t_{2g}-like orbitals is dominated by the ligands π bonding; π acceptor ligands stabilize these orbitals while π donors destabilize them. Since the stronger π acceptors are in the equatorial plane, one of the low-lying t_{2g}-like orbitals is stabilized relative to the two remaining t_{2g}-like orbitals, which remain nearly degenerate. If the splitting of the t_{2g}-like orbitals, the energy difference between the low-lying nondegenerate orbital and the two nearly degenerate orbitals, is large (see **3**) then the two metal 3d electrons will occupy the low-lying nondegenerate orbital, and the compound will be diamagnetic. Conversely, if the splitting is small, one metal 3d

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