the basis sets. The integration of the charge density was carried out using PROAIM,[32] and the bond orders were calculated using a modified version of BONDER.[7]

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Supplementary Material Available: Tables of calculated energies, structures, bond properties, and atom properties (35 pages). Ordering information is given on any current masthead page.

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Resonance Interactions in Acyclic Systems. 5. Structures, Charge Distributions, and Energies of Some Heterobutadiene Rotamers[†]

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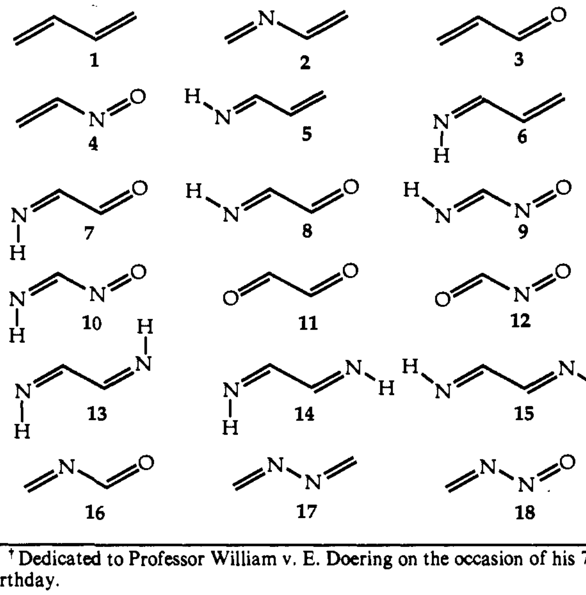
Abstract: The structures, energies, and rotational profiles of 17 heterobutadienes have been studied at the MP2/6-31G* theoretical level, with additional single point calculations at the MP3/6-311++G** level. The rotational profiles are, in part, determined by steric interactions between groups or between lone pairs. The magnitudes of these energies have been studied by examining the rotational profiles for some N-protonated derivatives which serve to minimize lone pair interactions. The conjugative interaction between the double bonds has been studied by examining the extent to which localized π orbitals have components at the other atoms and by calculation of bond orders as a function of torsional angle. The effect of a dipolar medium on the rotational barriers has been studied using reaction field theory. The atomic charges for the heterobutadienes have been calculated via numerical integration of the charge density within appropriately defined volume elements. In addition, the proton affinities and central bond dissociation energies have been calculated. The rotational barriers (s-trans to transition state) were largely a result of π-electron delocalization. However, shifts in π-electrons were compensated by shifts in σ-electrons so that the changes in total electron populations on rotation about the central bond were small.

1. Introduction

Butadiene and its heteroatom derivatives are common reagents in organic synthesis.[1] As such, it seemed useful to explore their structures and properties in greater detail than has been done so far. The magnitudes of the rotational barriers and the s-cis/s-trans relative energies were of particular interest to us because they may reveal the nature of the intramolecular interactions. The importance of π-resonance interactions also has been of special interest to us,[2] and these compounds present additional opportunities to examine these interactions.

The compounds included in this study are **1–18**, where only the trans forms are shown below. In the case of **5–10** and **13–15**, there are rotamers about the C=N bonds, and in each case both of the forms have been examined. This investigation is concerned with what may be learned about intramolecular interactions in these compounds via ab initio molecular orbital studies. The effect of replacing CH or CH_2 groups of butadiene by N, NH, or O will be examined by comparing structures, rotational barriers, degrees of π-electron delocalization, charge densities, and the effects of protonation and solvation in this series of compounds.

There have, of course, been many previous theoretical studies of these compounds. Butadiene (**1**)[2,3] and acrolein (**3**)[2,4] have been studied at a variety of theoretical levels, and the more recent calculations including correction for electron correlation in obtaining both the structures and energies are in very good agreement. Glyoxal (**11**) also has been studied at correspondingly high theoretical levels.[5] The azabutadienes (**2,5,6,13–15,17**) have



[†] Dedicated to Professor William v. E. Doering on the occasion of his 75th birthday.

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recently been studied by Bachrach and Liu at the MP2/6-31G*//HF/6-31G* level,[6] and there is a very recent report on some of these compounds at the HF/6-31G* level.[7]

The other compounds have received much less detailed study. Methyleneformamide (**16**) has been studied at the 3-21G level.[8] Nitrosoformaldehyde (**12**) has been studied at the 4-31G* level,[9] and nitrosoethylene (**4**) has been studied at the HF/6-31G*//HF/4-31G and MP2/4-21G//HF/4-31G levels.[10] With the nitroso compounds, only the planar conformers were examined. The azaacroleins (**7** and **8**) have been studied at the 4-31G* level,[9] but the nitrosomethanamines (**9** and **10**) and *N*-nitrosomethanamine (**18**) do not appear to have been the subject of previous theoretical studies.

2. Structures, Conformations, and Energies

In order to have a set of data obtained at a consistent theoretical level, geometry optimizations were carried out at the MP2/6-31G* level,[11] which usually gives quite good structural parameters. In the cases of butadiene (**1**), acrolein (**3**), glyoxal (**11**), and 2,3-diazabutadiene (**17**), experimental geometries are available[12] and agree with the MP2/6-31G* geometries obtained here with an average error of ±1° for bond angles and ±0.015 Å for bond lengths. The calculated energies for the stationary states along the rotational pathway are summarized in Table I, and data for additional torsional angles along with the full structural data in Z-matrix format are available as supplementary material. The bond angles and numbering schemes are shown in Figure 1. All calculations were performed using a development version of the GAUSSIAN 91 package of programs.[13]

Although the 6-31G* basis set, after correction for electron correlation, gives good structural data, the relative energies for compounds such as these often are significantly affected by basis set size. In order to obtain more satisfactory energies, we have carried out MP3/6-311++G** calculations at the MP2/6-31G* geometries. This basis set is effectively triple ζ for the valence electrons and includes both polarization functions and diffuse functions that are thought to be important for the proper description of lone pairs.[14] This level of theory has previously been applied to butadiene (**1**),[2,3] acrolein (**3**),[2] and glyoxal (**11**).[5] The energies thus obtained are included in Table I, along with the calculated dipole moments. The relative energies derived from the calculations must be corrected for zero-point energy changes before being compared with experimental data. Therefore, we have calculated the vibrational frequencies at the 6-31G* level for all of the stationary states. The zero-point energies derived from these calculations, after being scaled by the factor 0.90, are known to be in good agreement with those obtained from experimental data.[11] The data are included in Table I. The $\Delta\Delta H$ values are the relative energies at 0 K corrected for the changes in zero-point energies.

The rotational profiles derived from the calculations are summarized in Figure 2 and are generally in good agreement with the available experimental data (Table II). The solid lines give the MP3/6-311++G**//MP2/6-31G* relative energies, the short dashed lines give the MP2/6-31G* energies, and the long dashes give the HF/6-31G* energies. The calculated barriers for acrolein and glyoxal are in very good agreement with the experimental data. The torsional energy profile for butadiene (**1**) has been the subject of considerable controversy, with some experimental data favoring the cis rotamer as the higher energy conformer,[15] and most theoretical calculations favoring the gauche form, with the cis rotamer as a transition state separating the two gauche rotamers.[2,3] In view of the good agreement among the several high-level calculations for butadiene (barrier ~5 kcal/mol), it seems likely that the experimental barrier is too large (~7.5 kcal/mol). In particular, it seems unlikely that the barrier for butadiene would be *greater* than that for acrolein (**3**) (~6.5 kcal/mol). The experimental data for 2,3-diazabutadiene (**17**) are limited,[16] and the relative energy of the s-cis form is not accurately known. However, there is fair agreement between experiment and theory on the relative energy of the gauche rotamer.

The most remarkable feature of the rotational profiles for compounds **1–15** is their similarity. In each case, the ~90° rotamer has an energy 4–8 kcal/mol greater than that for the trans (180°) rotamer, and in most cases the energy drops significantly on going from 90° to 0°. One way in which to further explore the similarities is to transform the curves into their 1-fold, 2-fold and 3-fold components. These three terms of a Fourier expansion will fit each of the curves with little error, and the magnitudes of the terms are summarized in Table III. There is no assurance that the terms thus obtained will have any real physical significance because the intermolecular interactions may have a different functional form. Nevertheless, the Fourier analysis provides a systematic procedure for comparing these closely related compounds, and thus may be useful in at least a comparative sense.

One of the surprising observations is the relatively large 3-fold term for many of these compounds. An examination of Figure 2 and Table III shows that the 3-fold term is significant only in the cases where each of the terminal groups is either a methylene or an NH group with the H pointing "inward" in the s-cis conformer. Thus, butadiene (**1**) and 2-azabutadiene (**2**) have large 3-fold terms, but acrolein (**3**) and glyoxal (**11**) do not. This could arise from either steric or electronic factors. The strong dependence of the 3-fold term on the position of the H in the terminal NH groups (which will be further seen in the protonated compounds discussed below) suggests that primarily steric factors are involved. Furthermore, substituting fluorine for one or more of the hydrogens of butadiene has very little effect on the 3-fold term as calculated at the RHF/6-31G* optimized level of theory.[17] These substitutions would strongly affect the electronic characteristics of the molecule, but not its steric characteristics.

One possible explanation for the appearance of the 3-fold term is as follows. Both the s-cis and s-trans rotamers of butadiene and many of its heteroanalogues have unfavorable steric interactions. In butadiene, the close approach of H6 and H10 will dominate the s-cis form while the interactions of H6 and H8, and of H7 and H10 will adversely affect the s-trans conformer. The interaction of H6 and H10 in the s-cis form is very strong, as

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Table I. Calculated Energies of Heterobutadienes[a]

	τ^c	HF 6-31G*[d]	MP2 6-31G*	MP3 6-311++G**	E_{rel}	ZPE	$\Delta\Delta H$	μ_b
Butadiene (**1**)								
	0	−154.91346	−155.43599	−155.56127	3.59	51.53	3.42	0.025
min	37.7	−154.91481 (39)	−155.43744	−155.56317	2.40	51.68	2.38	0.069
TS	101.6	−154.90998 (102)	−155.43215	−155.55877	5.16	51.32	4.79	0.044
	180	−154.91965	−155.44171	−155.56699	0.00	51.70	0.0	0.000
2-Azabutadiene (**2**)								
	0	−170.90220	−171.45628	−171.57514	5.60	44.63	5.56	2.000
min	54.2	−170.90780 (55)	−171.46290	−171.56197	1.40	44.85	1.49	1.830
TS	111.0	−170.90418 (109)	−171.45880	−171.57896	3.29	44.42	2.94	2.075
	180	−170.91110	−171.46482	−171.58420	0.00	44.76	0.00	1.914
Acrolein (**3**)								
	0	−190.75977	−191.32624	−191.44652	2.24	37.55	2.26	3.267
TS	91.4	−190.74932 (92)	−191.31556	−191.43884	7.06	37.04	6.56	3.255
	180	−190.76242	−191.32858	−191.45009	0.00	37.53	0.00	4.007
Nitrosoethylene (**4**)								
	0	−206.67053	−207.27473	−207.39020	4.17	29.92	3.91	3.308
TS	93.8	−206.66264 (94)	−207.26566	−207.38400	8.06	29.60	7.49	2.723
	180	−206.67737	−207.28080	−207.39685	0.00	30.18	0.00	3.708
(*E*)-1-Azabutadiene (**5**)								
	0	−170.91603	−171.46995	−171.59208	2.27	45.14	2.16	1.921
TS	95.2	−170.90875 (96)	−171.46220	−171.58657	6.22	44.82	5.65	2.263
	180	−170.92052	−171.47404	−171.59649	0.00	45.25	0.00	2.500
(*Z*)-1-Azabutadiene (**6**)								
	0	−170.91389	−171.46838	−171.58998	3.03	45.11	2.88	2.961
min	31.7	−170.91474 (35)	−171.46909	−171.59123	2.25	45.26	2.25	2.901
TS	97.7	−170.90991 (99)	−171.46366	−171.58707	4.86	44.90	4.50	2.730
	180	−170.91913	−171.47269	−171.59481	0.00	45.26	0.00	3.095
(*Z*)-4-Azaacrolein (**7**)								
	0	−206.75396	−207.35374	−207.47121	0.50	31.07	0.69	2.793
TS	89.6	−206.74364 (92)	−207.34240	−207.46268	5.85	30.48	5.45	2.546
	180	−206.75406	−207.35283	207.47201	0.00	30.88	0.00	1.951
(*E*)-4-Azaacrolein (**8**)								
	0	−206.74729	−207.34651	−207.46578	5.82	30.74	5.62	4.892
TS	81.4	−206.74469 (89)	−207.34258	−207.46382	7.05	30.46	6.57	4.209
	180	−206.75803	−207.35555	−207.47505	0.00	30.94	0.00	2.728
(*E*)-*C*-Nitrosomethanimine (**9**)								
	0	−222.66304	−223.29896	−223.41390	4.23	23.27	3.98	3.921
min	38.9	−222.66415 (43)	−223.29999	−223.41528	3.36	23.44	3.28	3.935
TS	90.2	−222.66250 (90)	−223.29725	−223.41334	4.58	23.07	4.13	3.751
	180	−222.67122	−223.30599	−223.42064	0.00	23.52	0.00	3.467
(*Z*)-*C*-Nitrosomethanimine (**10**)								
	0	−222.66857	−223.30630	−223.41873	2.50	23.55	2.50	0.941
TS	88.9	−222.66241 (90)	−223.29823	−223.41302	6.08	23.08	5.61	0.857
	180	−222.67292	−223.30835	−223.42271	0.00	23.55	0.00	0.510
Glyoxal (**11**)								
	0	−226.58323	−227.19687	−227.31552	4.57	22.96	4.46	4.509
TS	78.5	−226.58075 (75)	−227.19265	−227.31281	6.27	22.62	5.81	3.791
	180	−226.59218	−227.20373	−227.32280	0.00	23.07	0.00	0.00
Nitrosoformaldehyde (**12**)								
	0	−242.50317	−243.15393	−243.26741	3.34	15.61	3.20	2.782
min	26.1	−242.50379 (45)	−243.15402	−243.26777	3.11	15.66	3.02	2.800
TS	82.0	−242.50344 (80)	−243.15273	−243.26712	3.53	15.37	3.14	2.715
	180	−242.50953	−243.15878	−243.27274	0.00	15.75	0.00	1.833
(*Z*,*Z*)-1,4-Diazabutadiene (**13**)								
	0	−186.90978	−187.49703	−187.61538	2.62	38.52	2.45	0.868
min	22.3	−186.91036 (31)	−187.49719	−187.61594	2.27	38.71	2.25	0.947
TS	93.0	−186.90596 (92)	−187.49187	−187.61216	4.64	38.39	4.34	0.811
	180	−186.91449	−187.50025	−187.61955	0.00	38.69	0.00	0.000
(*E*,*Z*)-1,4-Diazabutadiene (**14**)								
	0	−186.91504	−187.50155	−187.62007	0.80	38.78	1.47	3.844
TS	94.0	−186.90690 (95)	−187.49144	−187.61284	5.34	38.33	5.56	3.576
	180	−186.91621	−187.50144	−187.62135	0.00	38.11	0.00	3.262
(*E*,*E*)-1,4-Diazabutadiene (**15**)								
	0	−186.90684	−187.49263	−187.61314	7.19	38.41	6.85	4.090
min	28.0	−186.90711 (33)	−187.49283	−187.61389	6.72	38.50	6.47	4.003
TS	82.5	−186.90602 (80)	−187.49079	−187.61312	7.20	38.29	6.74	3.307
	180	−186.92001	−187.50459	−187.62459	0.00	38.75	0.00	0.000
Methyleneformamide (**16**)								
	0	−206.76020	−207.35616	−207.47018	2.10	30.65	1.94	2.006
min	51.3	−206.76120 (39)	−207.35866	−207.47352	0.00	30.81	0.00	2.990
TS	135.9	−206.75617 (126)	−207.35462	−207.47053	1.88	30.35	1.42	4.940
	180	−206.75775	−207.35525	−207.47094	1.62	30.62	1.44	5.295

Table I (Continued)

	τ^c	HF 6-31G*^{d}	MP2 6-31G*	MP3 6-311++G**	E_{rel}	ZPE	$\Delta\Delta H$	μ_b
			2,3-Diazabutadiene (**17**)					
	0	−186.859 55	−187.449 72	−187.561 98	16.30	37.45	15.90	4.319
	180	−186.886 00	−187.473 30	−187.587 95	0.00	37.84	0.00	0.000
			N-Nitrosomethanimine (**18**)					
	0	−222.650 10	−223.291 11	−223.398 10	7.67	22.81	7.40	2.955
min	72.5	−222.657 47 (71)	−223.298 10	−223.407 47	1.79	23.04	1.76	3.375
TS	118.8	−222.657 17 (102)	−223.297 32	−223.408 93	0.88	22.80	0.60	3.663
	180	−222.660 35	−223.298 29	−223.410 33	0.00	23.08	0.00	3.956

[a] Total energies are given in hartrees, relative energies and zero-point energies are given in kcal/mol. The HF/6-31G* energies were computed at the HF/6-31G* optimized geometries. The MP2/6-31G* and MP3/6-311++G** energies were obtained at the MP2/6-31G* geometries. All MOs were used in calculating the correlation energy for the MP2 optimizations, but the frozen core approximation was utilized for the MP3 single point calculations. The zero-point energies were obtained from HF/6-31G* calculations where the frequencies were scaled by 0.90. [b] The dipole moments (D) were calculated from the HF/6-311++G** density at the MP2/6-31G* geometry. [c] MP2 torsional angle values. [d] The HF angles (deg) are given in parentheses.

Table II. Comparison of Calculated and Experimental Torsional Parameters

compd	parameter	theory	expt	ref
butadiene	*E*(gauche)	2.4	2.1–3.0	*a*
	E(gauche-TS)	2.4	3.9	*b*
	E(trans-TS)	4.8	7.2–7.6	*c,d*
acrolein	*E*(cis)	2.3	1.6–2.2	*e,f*
	E(TS)	6.6	6.5–7.0	*f*
glyoxal	*E*(cis)	4.5	3.2–3.9	*d,g*
	E(TS)	5.8	5.1	*d*
2,3-diazabutadiene	*E*(TS)		1.5	*h*
	E(gauche)	2.2	1.2	*h*

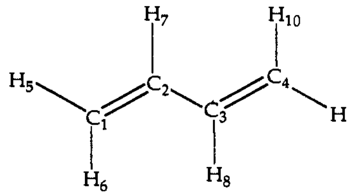
[a] Compton, D. A. C.; George, W. O.; Maddams, W. F. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1662. Lipnick, R. L.; Garbish, E. W., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6370. Aston, J. G.; Szasz, G.; Woolley, H. W.; Brickwedde, F. G. *Chem. Phys.* **1946**, *14*, 67. [b] Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657. [c] Carreira, L. A. *J. Chem. Soc.* **1975**, *62*, 3851. [d] Durig, J. R.; Bucy, W. E.; Cole, A. R. H. *Can. J. Phys.* **1976**, *53*, 1832. [e] Blom, C. E.; Muller, R. P.; Günthard, Hs. H. *Chem. Phys. Lett.* **1980**, *73*, 483. Bair, E. J.; Goetz, W.; Ramsay, D. A. *Can. J. Phys.* **1971**, *49*, 2710. Alves, A. C. P.; Christoffersen, J.; Hollas, J. M. *Mol. Phys.* **1971**, *20*, 625; **1971**, *21*, 384. [f] DeGroot, M. S.; Lamb, J. *Proc. Roy. Soc. London, Ser. A* **1957**, *242*, 36. Brand, J. C. D.; Williamson, D. G. *Disc. Faraday Soc.* **1963**, *35*, 184. [g] Currie, G. N.; Ramsay, D. A. *Can. J. Phys.* **1971**, *49*, 317. Butz, K. W.; Johnson, J. R.; Krajnovich, D. J.; Parmenter, C. S. *J. Chem. Phys.* **1987**, *86*, 5923. [h] Hagen, K.; Bondybey, V. E.; Hedberg, K. *J. Am. Chem. Soc.* **1977**, *99*, 1365.

Table III. Terms of Cosine Fourier Series Expansions for Calculated Torsional Potentials[a]

	term			
compd	constant	1-fold	2-fold	3-fold
butadiene (**1**)	3.03	1.30	−3.09	2.26
2-azabutadiene (**2**)	2.40	2.47	0.31	3.24
acrolein (**3**)	3.82	1.63	−5.93	0.62
nitrosoethylene (**4**)	4.67	2.72	−5.93	1.48
(*E*)-1-azabutadiene (**5**)	3.54	1.56	−4.78	1.22
(*Z*)-1-azabutadiene (**6**)	2.81	1.26	−3.26	1.70
(*Z*)-4-azaacrolein (**7**)	2.83	0.52	−5.46	−0.02
(*E*)-4-azaacrolein (**8**)	4.72	5.40	−3.94	0.40
(*E*)-*C*-nitrosomethanimine (**9**)	3.00	2.88	−2.26	1.28
(*Z*)-*C*-nitrosomethanimine (**10**)	3.45	2.24	−4.82	0.24
glyoxal (**11**)	4.02	4.50	−3.76	0.06
nitrosoformaldehyde (**12**)	2.45	2.76	−1.85	0.53
(*Z,Z*)-1,4-diazabutadiene (**13**)	2.71	1.54	−3.36	0.98
(*E,Z*)-1,4-diazabutadiene (**14**)	2.69	0.24	−4.90	0.56
(*E,E*)-1,4-diazabutadiene (**15**)	5.11	6.16	−3.50	0.90
methyleneformamide (**16**)	1.15	−0.97	1.19	1.46
2,3-diazabutadiene (**17**)	4.45	12.03	6.41	4.27
N-nitrosomethanimine (**18**)	4.67	5.99	2.44	1.60

[a] Based on the MP3/6-311++G* energies. All values are in kcal/mol and refer to the potential form: $E = a + (b/2)\cos\tau + (c/2)\cos 2\tau + (d/2)\cos 3\tau$.

indicated by the large C–C–C bond angles (see Figure 1), but it should drop off rapidly as the torsional angle moves away from 0°. The unfavorable interactions in the s-trans form are weaker, but they might be expected to drop off less rapidly as the torsional angle moves away from 180°. The reason is that H6 and H10 are farther from the axis of torsion (the C–C bond) than are H7 and H8. Consequently, changes in the torsional angle have a larger affect on the H6-H10 distance than on the other H–H distances.



Based on this line of reasoning, one might make the following prediction: although the s-cis rotamer is higher in energy than the s-trans, the steric interactions dominant in the s-trans form are more important in the vicinity of 90° than are those of the s-cis form. Thus, one might expect that steric interactions would be minimized at an angle *less* than 90°, leading to a transition state angle *greater* than 90°. The lopsided steric potential, superimposed on a 2-fold term representing the π-electron interaction, would lead to an overall torsional potential similar to that which is observed. A similar argument can be made for 2-azabutadiene, in which the small C–N–C bond angle (116.5°, as opposed to 123.7° for the C–C–C angle in butadiene) exacerbates the steric repulsion between H6 and H7 in the s-trans conformer. The large change in the N–C–H7 bond angle upon rotation reflects the strength of this interaction (from 111.9° in the s-cis conformer to 118.3° in the s-trans conformer; see Figure 1). An attempt was made to examine the above hypothesis via rigid rotor calculations, but the results were inconclusive.

In some cases, such as glyoxal (**11**) and 2,3-diazabutadiene (**17**), there is a large increase in dipole moment in going from the s-trans to the s-cis rotamer. It results from the additive alignment of the C═O or C═N dipoles in the cis form, and this in turn leads to a repulsive Coulombic interaction. With **11**, most of the difference in energy between cis and trans must be due to this effect, but with **17**, there is an additional destabilizing interaction, the repulsion between the nitrogen lone pairs in the cis form. The compounds **8**, **9**, and **15** also have higher energies for the s-cis rotamers than one might expect on the basis of dipolar interactions alone. It seems likely that this is caused by a repulsive interaction between the lone pairs of the terminal groups. The data suggest that this repulsion is greater for lone pairs on nitrogen than for those on oxygen, which is in accord with their greater basicity.

The lone pair–lone pair interaction is readily seen in examining the torsional profiles for **17** and **18**, and presumably is a large factor in determining the differences between **13**, **14**, and **15**. One of the lone pairs in these compounds may be effectively eliminated

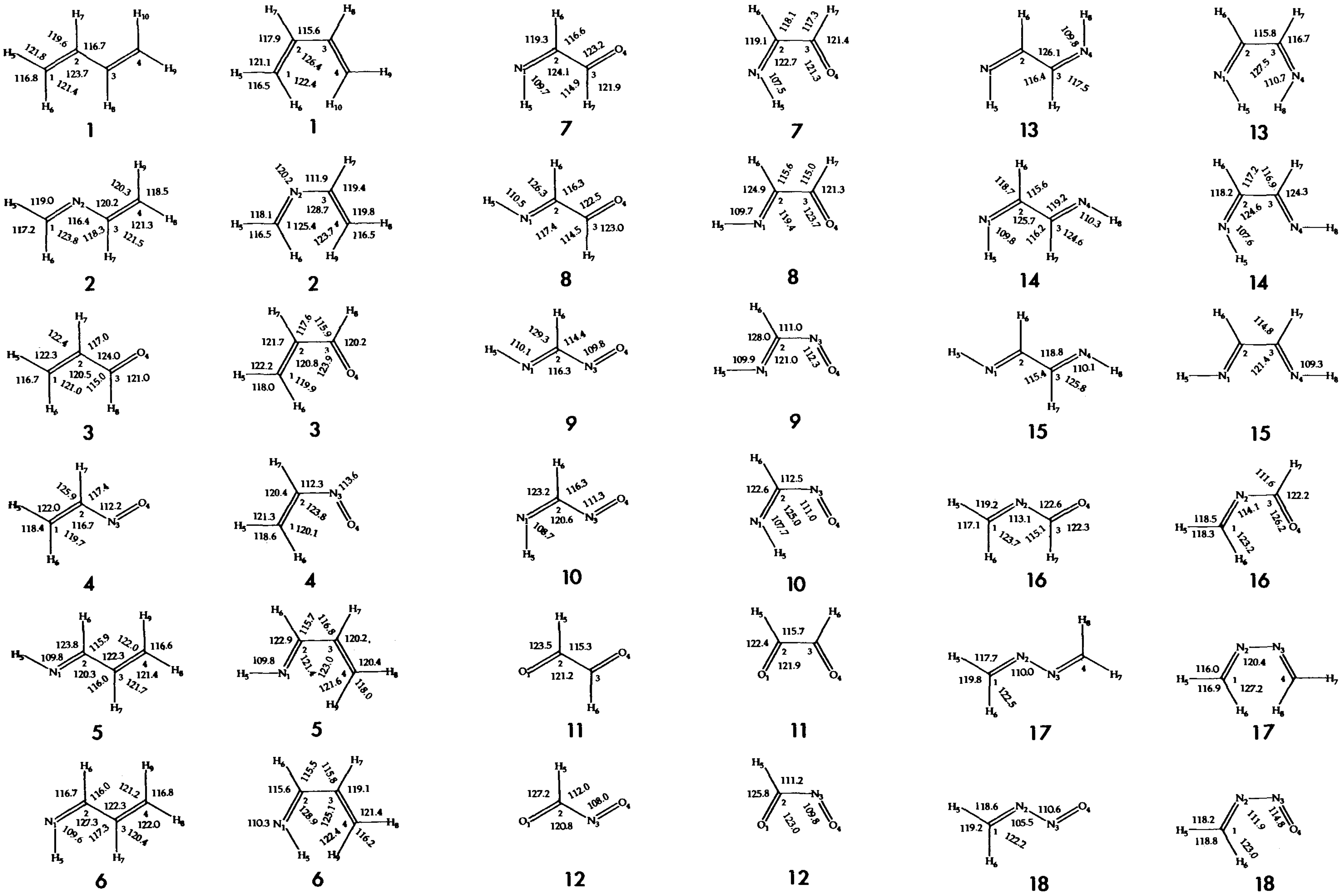


Figure 1. Bond angles for butadiene and the heterobutadienes.

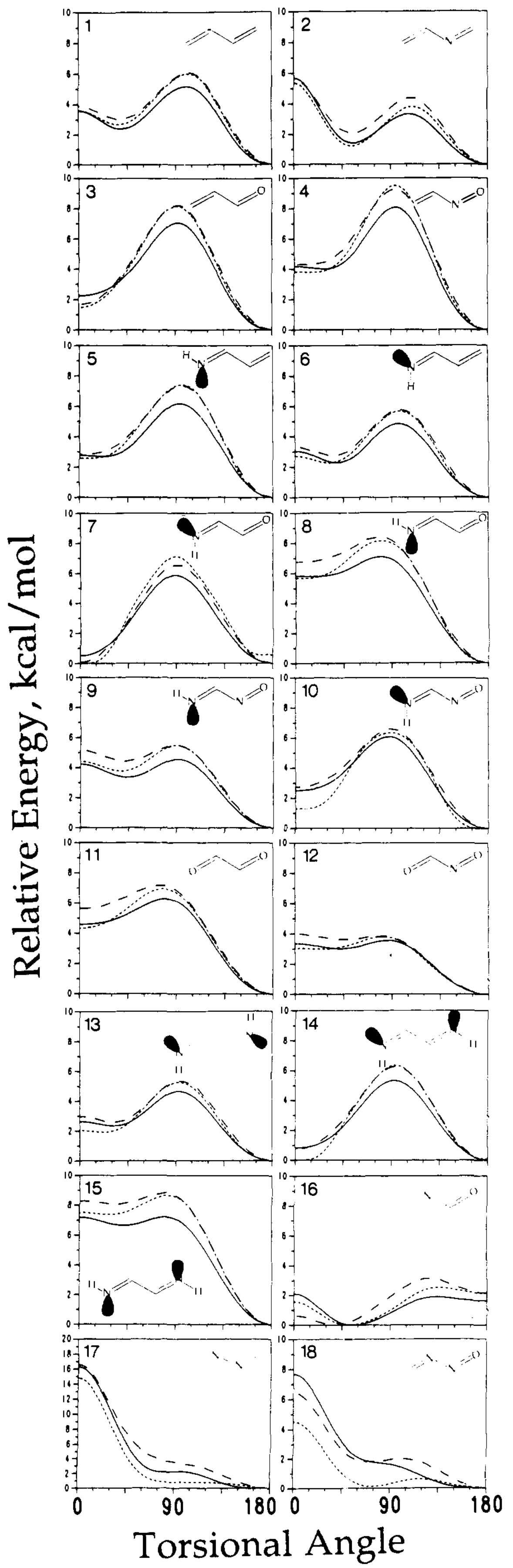


Figure 2. Rotational profiles for butadiene and the heterobutadienes. The solid line gives the MP3/6-311++G** relative energies, the long dashes give the MP2/6-31G* energies, and the short dashes give the HF/6-31G* relative energies.

Table IV. Calculated Energies of N-Protonated Heterobutadienes[a]

	τ (deg)	HF/6-31G* (hartrees)	*E*(rel) (kcal/mol)
		2-Azabutadiene (**2**)	
	0	−171.26551	3.82
min	49.8	−171.26821	2.12
TS	104.5	−171.26577	3.65
	180	−171.27159	0.00
		Nitrosoethylene (**4**)	
	0	−206.98426	1.41
TS	93.2	−206.96645	12.58
	180	−206.98650	0.00
		1-Azabutadiene (**5** and **6**)	
	0	−171.28875	5.12
TS	96.1	−171.27866	11.45
	180	−171.29691	0.00
		4-Azaacrolein (**7** and **8**)	
	0	−207.09661	0.00
TS	96.7	−207.08682	6.14
	180	−207.09147	3.23
		C-Nitrosomethanimine (**9** and **10**)	
	0	−222.99362	2.62
TS	93.1	−222.99231	3.45
	180	−222.99779	0.00
		Nitrosoformaldehyde (**12**)	
	0	−242.78158	3.54
TS	79.1	−242.77592	7.09
	180	−242.78722	0.00
		(*Z*)-1,4-Diazabutadiene (**13** and **14**)	
	0	−187.25652	4.71
TS	94.4	−187.25497	5.68
	180	−187.26402	0.00
		(*E*)-1,4-Diazabutadiene (**14** and **15**)	
	0	−187.27918	0.00
TS	97.6	−187.26579	8.40
	180	−187.27600	2.00
		1,4-Diazabutadiene (diprotonated)	
	0	−187.42264	6.76
	180	−187.43342	0.00
		Methyleneformamide (**16**)	
	0	−207.09975	0.00
TS	92.8	−207.08607	8.59
	180	−207.09667	1.93
		2,3-Diazabutadiene (**17**)	
	0	−187.22267	8.49
min	69.4	−187.22863	4.76
	180	−187.23621	0.00
		N-Nitrosomethanimine (**18**)	
	0	−222.94791	0.50
min	32.3	−222.94871	0.00
TS	121.8	−222.94049	5.15
	180	−222.94379	3.09

[a] The energies were calculated at the HF/6-31G* optimized geometries.

by protonation at nitrogen, and this should have a marked effect on the rotational profile. Protonation may also affect some of the other compounds, and a number of them have been examined. The energies of 6-31G* optimized structures are given in Table IV, and the relative energies are shown in Figure 3. Data for additional torsional angles are given in the supplementary material. In each case, the normal form is shown with a solid line, and the protonated form is shown with a dashed line. In some cases, two of the heterobutadienes give the same protonated form, and in these cases the second compound is shown with long dashes.

The protonation of 2,3-diazabutadiene (**17**) led to a marked decrease in the relative energy of the cis form, along with a small increase in the energy of the 90° rotated form. The 8 kcal/mol change in the cis relative energy clearly shows that lone pair repulsion is a major force with this compound. It is, of course,

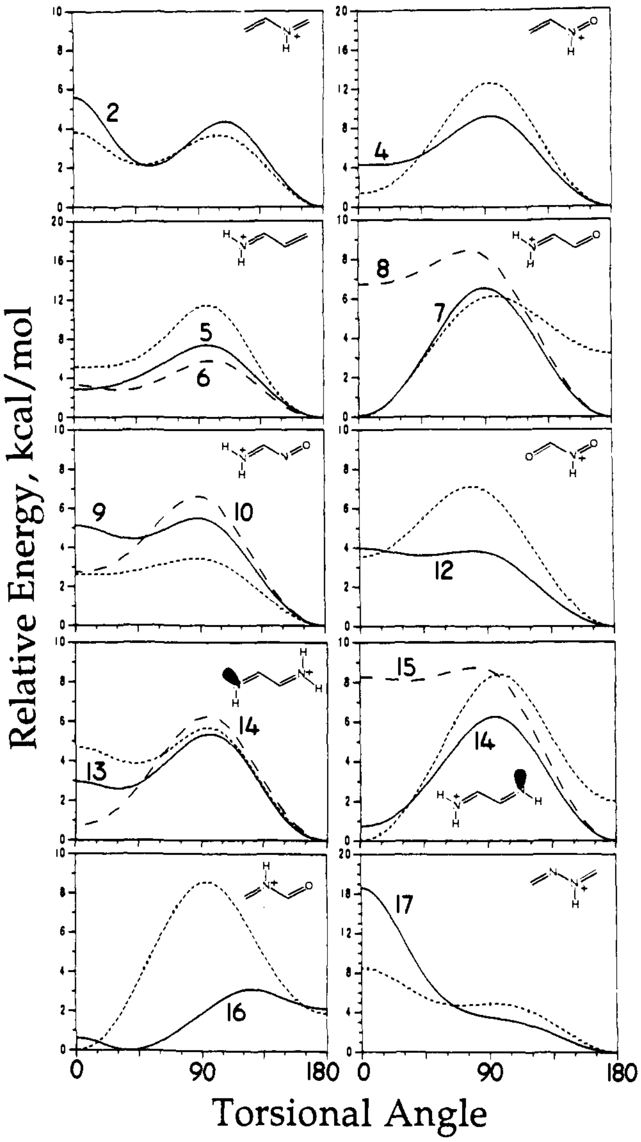


Figure 3. Rotational profiles for the protonated heterobutadienes. The solid line gives the HF/6-31G* relative energies for the parent compound and the short dashes give the energies for the protonated form. In the cases where two heterobutadienes give the same conjugate acid, the second parent compound is shown with short dashes.

not surprising since hydrazine also has a large lone-pair interaction energy (rotational barrier for hydrazine = 8.95 kcal/mol at MP3/6-311++G**//MP2/6-31G* after RHF/6-31G* ZPE correction). Protonation of **8** and **15** eliminates the cis-repulsive interaction between the lone pairs at the terminal atoms and markedly decreases the energy of the cis forms. With 2-azabutadiene (**2**), there also is a small decrease in the cis relative energy on protonation. Here, protonation changes the C–N–C bond angle from 121.8° to 129.3° and moves the terminal methylene groups apart, leading to a smaller steric interaction. In the cases where protonation leads to a structure in which hydrogen–hydrogen repulsion is present in the s-cis and s-trans forms, an apparent 3-fold barrier term appears in the rotational profile. Here, the similarities between butadiene (**1**) and protonated **5** and **6**, and **13** and **14** might be noted.

Methyleneformamide (**16**) is unusual among the compounds studied in that the dipole moment of the s-cis form is lower than that of the s-trans. This factor would account for the lower relative energy of the s-cis form, and steric interactions could account for the small increase in energy with respect to gauche. The lone pair on nitrogen competes with the C=C bond for interaction with the carbonyl group, leading to a small change in energy from 180° to 90°. The lone pair must rehybridize in the 90° conformer in order to optimize its interaction with the C=O π-system, and the variation of the C–N–C bond angle reflects this process: it changes from 114.1° in the s-cis conformer to 120.0° in the 90° conformer and back to 113.1° in the s-trans conformer. Protonation of **16** led to a complete change in the rotational profile, with the minimum at 40° being eliminated, and the rotational barrier being markedly increased. Protonated **16** now resembles acrolein (**3**). These data clearly show that the nitrogen lone pair is the structural feature responsible for the unusual rotational profile of **16**.

Table V. Calculated Proton Affinities of the s-Trans Rotamers (HF/6-31G*)[a]

compd	energy (hartrees)	protonated energy (hartrees)	PA (kcal/mol)
2-azabutadiene (**2**)	−170.911 10	−171.271 59	226.2
nitrosoethylene (**4**)	−206.677 37	−206.986 50	194.0
(*E*)-1-azabutadiene (**5**)	−170.920 52	−171.296 91	236.2
(*Z*)-1-azabutadiene (**6**)	−170.919 13	−171.296 91	237.0
(*Z*)-4-azaacrolein (**7**)	−206.754 06	−207.091 47	211.7
(*E*)-4-azaacrolein (**8**)	−206.758 03	−207.091 47	209.2
(*E*)-*C*-nitrosomethanimine (**9**)	−222.671 22	−222.997 79	204.9
(*Z*)-*C*-nitrosomethanimine (**10**)	−222.672 92	−222.997 79	203.9
nitrosoformaldehyde (**12**)	−242.509 53	−242.787 22	174.3
diazabutadiene (**13**-*Z*)	−186.914 49	−187.264 02	219.3
diazabutadiene (**14**-*Z*)	−186.916 21	−187.264 02	218.3
diazabutadiene (**15**-*Z*)	−186.920 01	−187.264 02	215.9
diazabutadiene (**13**-*E*)	−186.914 49	−187.276 00	226.9
diazabutadiene (**14**-*E*)	−186.916 21	−187.276 00	225.8
diazabutadiene (**15**-*E*)	−186.920 01	−187.276 00	223.4
methyleneformamide (**16**)	−206.757 75	−207.096 67	212.7
2,3-diazabutadiene (**17**)	−186.886 00	−187.236 21	219.8
N-nitrosoimine (**18**)	−222.660 35	−222.943 79	177.9

[a] The energies were calculated at the HF/6-31G* optimized geometries.

The data thus obtained also allow an estimate of the proton affinities of the compounds, and they are summarized in Table V. Although a higher level of theory would probably be needed in order to obtain accurate values, and corrections for changes in zero-point energies should be made, the calculated values should prove useful at least in a comparative sense. The proton affinity of *N*-nitrosomethanimine (**18**) was computed only for protonation on the nitroso nitrogen; protonation on the imino nitrogen led to disintegration of the molecule. One might expect that the proton affinity of the lone pair on nitrogen would decrease with increasing substitution by electronegative atoms, and indeed this is observed. 2-Azabutadiene (**2**), which has only one electronegative atom, has the greatest proton affinity. Direct attachment of an oxygen atom, forming a nitroso group, causes a drastic reduction in the proton affinity. The three compounds in which a nitroso group becomes protonated (**4**, **12**, and **18**) have the three lowest proton affinities, all at least 30 kcal/mol less than that of 2-azabutadiene. More remote substitution by an oxygen atom, as in methyleneformamide (**16**), or substitution by nitrogen, as in 2,3-diazabutadiene (**17**), causes more moderate reductions. It is interesting to note that 2,3-diazabutadiene has a substantially greater proton affinity than does *N*-nitrosomethanimine (**18**) and also a much greater energy in the s-cis conformation. That the more basic lone pairs lead to the stronger repulsive interaction agrees well with expectations.

3. Interaction between π-Systems

The difference in energy between the 90° and 180° forms presumably arises mainly from an interaction between the two π-systems, which will be a maximum at 0° and at 180°. We have previously examined the details of such an interaction for butadiene (**1**),[2] and here it was found that the π-electron density at the C2–C3 bond was indeed somewhat greater for the 0° and 180° forms than for 90°, but also the σ-electrons were found to move in the opposite direction in order to minimize electron repulsion. As a result, the change in the net C–C bond strength on rotation, as judged by stretching force constants, was relatively small.

We were interested in developing a convenient and systematic way in which to examine the delocalization of the π-electrons. One way in which to accomplish this is to localize the π-bonds.

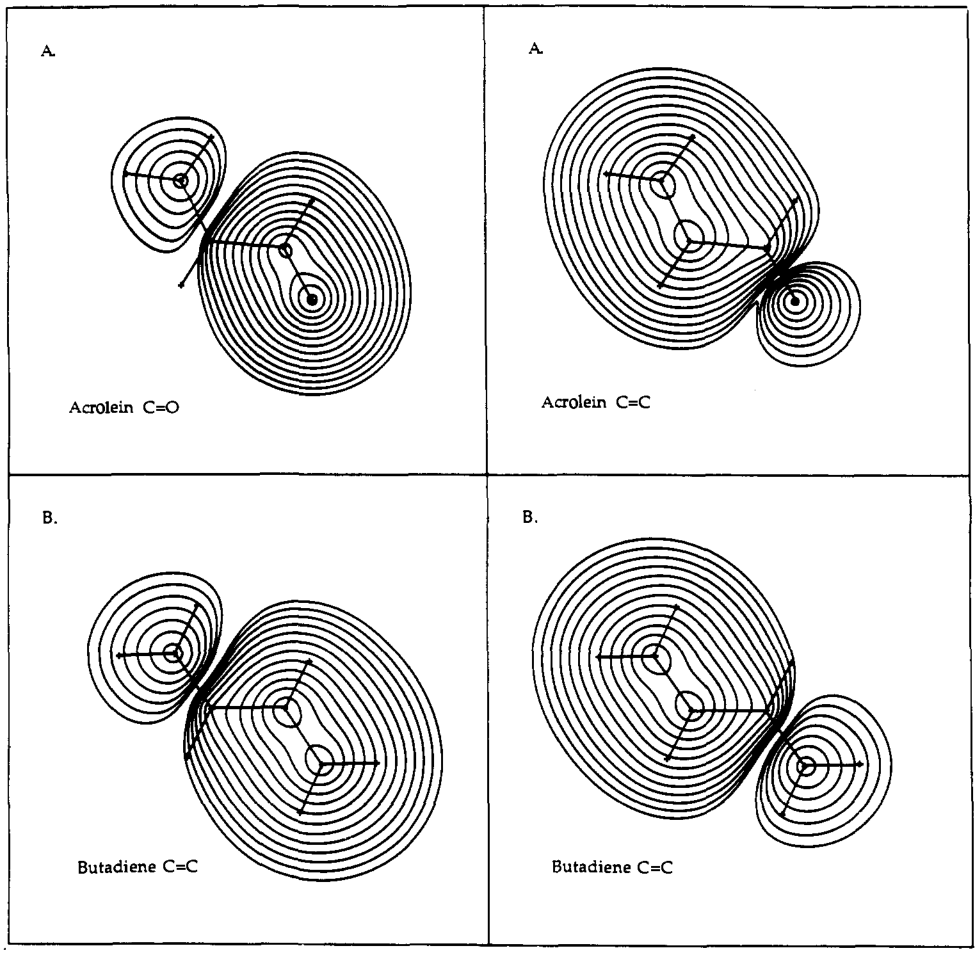


Figure 4. Electron density projection plots of localized π-bond orbitals for (a) acrolein and (b) butadiene. The lowest contour is 1×10^{-4} e/au^2, and the contours increase by a factor of 2 thereafter.

The inability of an orbital to be localized is a direct consequence of the bonding character it possesses and should provide a semiquantitative measure of delocalization. In the absence of a π-interaction across the central σ-bond, the localized π-bonds would reside entirely on one half of the molecule.[18] However, if there is a delocalized π-interaction, the localized orbitals will have some contribution from all of the centers. This approach has philosophical similarities to both the natural bond orbital method of Reed and Weinhold[19] and Cioslowski and Mixon's definition of bond order.[20] We have carried out Boys localizations[21] of the π-orbitals from the RHF/6-311++G**//MP2/6-31G* wave functions using the built-in capability of the GAUSSIAN 91 package of programs,[13] and examples of localized π-orbitals are shown in Figure 4. Some delocalization was found with butadiene (**1**), and with nitrosoethylene (**4**), there is considerable delocalization of the C=C bond into the N=O bond, but little reverse delocalization. Likewise in acrolein (**3**) donation is almost entirely from the C=C bond into the C=O antibond and not in the reverse direction.

In order to obtain a more quantitative measure of delocalization, we have calculated the fraction of charge transfer from the primary locus of the double bond to the other associated atoms. We have designated this quantity as the delocalization index, defined as the fraction of charge in a localized MO which resides on the "wrong" half of the molecule. The results of this analysis are given in Table VI. The atomic populations were calculated by integrating the electron density in each of the atomic basins as defined by Bader's topological theory of atoms in molecules.[22] This integration can be performed separately for each orbital of a localized wave function, such that the atomic populations that one obtains are broken down into the contributions from each of the orbitals. Thus one can define the population on each atom *for a single localized orbital.* The delocalization index of an orbital, then, is computed as the sum of the populations of the orbital on the atoms comprising the fragment of the molecule where the double bond does *not* reside divided by the sum of the populations of the orbital over all atoms. The sum over all atoms should of course be exactly two for a properly integrated orbital from a Hartree–Fock wave function. As an illustrative example, the delocalization index for the C=C π-bond of acrolein (**3**) is the total integrated density of the C=C π-bond orbital on the formyl group (C, H, and O, the "wrong" half of the molecule for the C=C bond) divided by the density over all space (=2.0000). Analogously, the delocalization index for the C=O π-bond is the density of the C=O π-orbital on the vinyl group divided by 2.0000.

The π-delocalization indices present a consistent picture. A C=C double bond has the highest polarizability of those in this

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(17) The torsional profiles for 2-fluoro-1,3-butadiene, 1,1-difluoro-1,3-butadiene, 2,3-difluoro-1,3-butadiene, 1,1,2-trifluoro-1,3-butadiene, 1,1,3-trifluoro-1,3-butadiene, 1,1,4,4-tetrafluoro-1,3-butadiene, (*E*)-1,3-pentadiene, (*Z*)-1,3-pentadiene, and 2-methyl-1,3-butadiene calculated at the RHF/6-31G* optimized level of theory are included in the supplementary material. See also Ribeiro-Claro, P. J. A. *Chem. Phys. Lett.* **1992**, *188*, 303.

(18) This is not precisely correct. As Professor Jerzy Cioslowski has pointed out (private communication), any real orbital can only approach zero in any finite region of space. It cannot have a value of zero except at a nodal point, line, or plane. Even a "perfectly" localized orbital will always have a decaying "tail" in the regions of all the other nuclei. In other words, strictly localized orbitals are nonphysical. However, the imprecise statement given above provides a clearer explanation and will suffice for the semiquantitative discussion which follows.

(19) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066.

(20) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142.

(21) Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296.

(22) (a) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990. (b) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9. (c) Srebrenik, S.; Bader, R. F. W. *J. Chem. Phys.* **1974**, *61*, 2536.

Table VI. Results of Boys Localizations[a]

bonds	τ (deg)	deloc index			
		Butadiene (1)			
		C=C			
$\sigma + \pi$	0	0.0210			
$\sigma + \pi$	90	0.0170			
$\sigma + \pi$	180	0.0242			
π	0	0.0360			
π	180	0.0419			
		2-Azabutadiene (2)			
		C=N	C=C	LP on N	
$\sigma + \pi$	0	0.0175	0.0291	0.0169	
$\sigma + \pi$	90	0.0142	0.0253	0.0273	
$\sigma + \pi$	180	0.0188	0.0355	0.0208	
π	0	0.0294	0.0475		
π	180	0.0318	0.0591		
		Acrolein (3)			
		C=O	C=C		
$\sigma + \pi$	0	0.0086	0.0314		
$\sigma + \pi$	90	0.0077	0.0180		
$\sigma + \pi$	180	0.0094	0.0317		
π	0	0.0141	0.0562		
π	180	0.0157	0.0570		
		Nitrosoethylene (4)			
		N=O	C=C	LP on N	
$\sigma + \pi$	0	0.0085	0.0429	0.0146	
$\sigma + \pi$	90	0.0079	0.0255	0.0178	
$\sigma + \pi$	180	0.0096	0.0511	0.0181	
π	0	0.0134	0.0752		
π	180	0.0155	0.0902		
		(*E*)-1-Azabutadiene (5)			
		C=N	C=C		
$\sigma + \pi$	0	0.0142	0.0274		
$\sigma + \pi$	90	0.0117	0.0183		
$\sigma + \pi$	180	0.0157	0.0278		
π	0	0.0238	0.0481		
π	180	0.0269	0.0492		
		(*Z*)-1-Azabutadiene (6)			
		C=N	C=C		
$\sigma + \pi$	0	0.0135	0.0228		
$\sigma + \pi$	90	0.0121	0.0184		
$\sigma + \pi$	180	0.0156	0.0271		
π	0	0.0229	0.0395		
π	180	0.0269	0.0477		
		(*Z*)-4-Azaacrolein (7)			
		C=N	C=O		
$\sigma + \pi$	0	0.0182	0.0096		
$\sigma + \pi$	90	0.0122	0.0079		
$\sigma + \pi$	180	0.0192	0.0102		
π	0	0.0319	0.0161		
π	180	0.0338	0.0173		
		(*E*)-4-Azaacrolein (8)			
		C=N	C=O		
$\sigma + \pi$	0	0.0199	0.0092		
$\sigma + \pi$	90	0.0127	0.0079		
$\sigma + \pi$	180	0.0197	0.0098		
π	0	0.0353	0.0151		
π	180	0.0353	0.0166		
		(*E*)-*C*-Nitrosomethanimine (9)			
		C=N	N=O	LP on N3	
$\sigma + \pi$	0	0.0225	0.0094	0.0157	
$\sigma + \pi$	90	0.0182	0.0084	0.0186	
$\sigma + \pi$	180	0.0283	0.0102	0.0174	
π	0	0.0380	0.0149		
π	180	0.0487	0.0167		
		(*Z*)-*C*-Nitrosomethanimine (10)			
		C=N	N=O	LP on N3	
$\sigma + \pi$	0	0.0230	0.0087	0.0154	
$\sigma + \pi$	90	0.0175	0.0084	0.0186	
$\sigma + \pi$	180	0.0294	0.0098	0.0188	
π	0	0.0397	0.0136		
π	180	0.0512	0.0160		
		Glyoxal (11)			
		C=O			
$\sigma + \pi$	0	0.0103			
$\sigma + \pi$	90	0.0081			
$\sigma + \pi$	180	0.0108			
π	0	0.0175			
π	180	0.0186			
		Nitrosoformaldehyde (12)			
		C=O	N=O	LP on N	
$\sigma + \pi$	0	0.0112	0.0098	0.0161	
$\sigma + \pi$	90	0.0114	0.0084	0.0194	
$\sigma + \pi$	180	0.0134	0.0109	0.0172	
π	0	0.0182	0.0158		
π	180	0.0224	0.0181		
		(*Z*,*Z*)-1,4-Diazabutadiene (13)			
		C=N			
$\sigma + \pi$	0	0.0156			
$\sigma + \pi$	90	0.0126			
$\sigma + \pi$	180	0.0171			
π	0	0.0270			
π	180	0.0300			
		(*E*,*Z*)-1,4-Diazabutadiene (14)			
		C=N	C=N		
$\sigma + \pi$	0	0.0176	0.0153		
$\sigma + \pi$	90	0.0123	0.0126		
$\sigma + \pi$	180	0.0170	0.0176		
π	0	0.0306	0.0258		
π	180	0.0295	0.0309		
		(*E*,*E*)-1,4-Diazabutadiene (15)			
		C=N			
$\sigma + \pi$	0	0.0165			
$\sigma + \pi$	90	0.0122			
$\sigma + \pi$	180	0.0175			
π	0	0.0284			
π	180	0.0304			
		Methyleneformamide (16)			
		C=O	C=N	LP on N	
$\sigma + \pi$	0	0.0115	0.0246	0.0179	
$\sigma + \pi$	90	0.0137	0.0144	0.0372	
$\sigma + \pi$	180	0.0140	0.0246	0.0195	
π	0	0.0179	0.0431		
π	180	0.0225	0.0433		
		2,3-Diazabutadiene (17)			
		C=N	LP on N		
$\sigma + \pi$	0	0.0187	0.0191		
$\sigma + \pi$	90	0.0187	0.0346		
$\sigma + \pi$	180	0.0224	0.0249		
π	0	0.0296			
π	180	0.0365			
		N-Nitrosomethanimine (18)			
		N=O	C=N	LP on N3	LP N2
$\sigma + \pi$	0	0.0073	0.0218	0.0189	0.0182
$\sigma + \pi$	90	0.0111	0.0195	0.0244	0.0468
$\sigma + \pi$	180	0.0100	0.0302	0.0260	0.0221
π	0	0.0103	0.0358		
π	180	0.0153	0.0520		

[a] The calculations were based on RHF/6-311++G** wave functions obtained at the MP2/6-31G* geometries.

study, and it gives the largest delocalization into the adjacent double bond. The % π-delocalization depends on the electronegativity of the adjacent bond, and for the trans rotamers it increases in the order: C=C, 4.2%; C=N, 4.9%; C=O, 5.7%; N=C, 5.9%; and N=O, 9.0%. For the symmetrical compounds, it decreases from 4.2% for C=C to 3.7% for N=C, 3.3% for C=N and 1.9% for C=O, reflecting the decreasing donating ability in this series.

Any analysis that relies on a σ–π separation cannot apply to nonplanar rotamers of butadiene analogues. However, the localization technique described above does not require this decomposition. If all the valence canonical orbitals from the Hartree–Fock wave function are localized, each of the resulting orbitals can easily be identified as a particular lone pair or two-center bond. The delocalization index is defined as before, but is tabulated only for those orbitals corresponding to bonds between the doubly bonded atoms. Between any given pair of doubly bonded atoms there are always two such orbitals, each representing a hybrid "σ/π" orbital reminiscent of a τ bond. These "total" delocalization indices describe the combined σ- and π-density, and thus are not directly comparable to the pure π-delocalization indices discussed earlier. In general, they have considerably lower values, since the more highly localized σ-bonds are included along with the π-bonds. However, it is now possible to observe the changes which occur upon rotation to 90°. The delocalization indices are also listed for the lone pairs on some of the nitrogen atoms.

In almost all cases, the delocalization indices for the double bonds are greater in the planar rotamers than in the 90° rotamer, in some instances by as much as a factor of 2. In butadiene (**1**), the delocalization index for the C═C bonds goes from 0.0242 in the s-trans rotamer to 0.0170 in the 90° rotamer. For acrolein (**3**), the C═C delocalization index goes from 0.0317 to 0.0180. The most marked decrease is for nitrosoethylene (**4**), in which the C═C π-bond is able to donate into the highly electron-accepting nitroso group: the delocalization index for the C═C bonds decreases from 0.0511 to 0.0255. The delocalization index for the N═O bonds remains nearly constant and quite small (~ 0.0090), as expected. At the other extreme, the delocalization indices for the C═O bonds of glyoxal (**11**) only vary between 0.0108 and 0.0081 as the molecule twists about the C—C bond. In fact, the presence of a significant barrier between the s-cis and s-trans rotamers of glyoxal remains somewhat of a mystery. The calculated charges, bond orders, delocalization indices, and intuition all strongly suggest that any π-delocalization interaction should be very weak.

The heterobutadienes with a nitrogen atom in one of the "inner" positions have a lone pair which lines up with the π-system of the adjacent fragment in the 90° rotamer. One might expect this lone pair to donate into the adjacent π^*-orbital, and indeed this is observed. The lone pair on the nitrogen of 2-azabutadiene (**2**) has a delocalization index of 0.0208 in the s-trans form, which increases to 0.0273 in the 90° form. This increase is half as large as the decrease in the delocalization indices of the C═C and C═N bonds upon rotation and provides a convenient explanation for the fairly low torsional barrier (3.3 kcal/mol, at 111°). The lone pair on the nitrogen atom of methyleneformamide (**16**) can donate into the C═O system, which is a much stronger acceptor than the C═C system of 2-azabutadiene. Consequently the delocalization index of the lone pair increases more, from 0.0195 to 0.0372, as the molecule rotates from 180° to 90°. This observation ties in nicely with the fact that methyleneformamide is the one heterobutadiene in this study that has a gauche (51°) conformer as its global energy minimum. The interaction of the lone pair with the C═O bonds would stabilize this conformer. The other compound in which a lone pair can donate into a strong π-acceptor in the 90° rotamer is *N*-nitrosomethanimine (**18**). It has a gauche minimum at 73° that is only 1.8 kcal/mol above the global minimum at 180° despite the large repulsions in the nearby s-cis rotamer.

One would not expect the lone pair on the nitrogen of a nitroso group to act as a good donor, and the delocalization indices uphold this view. For instance, the nitrogen lone pair in nitrosoethylene (**4**) has a delocalization index of 0.0181 in the s-trans form, which changes only to 0.0178 in the 90° rotamer. Even the nitrogen lone pair in nitrosoformaldehyde (**12**) only increases from 0.0172 to 0.0194 upon rotation to 90°, despite the strong electron accepting properties of the carbonyl group. *All* the nitrogen lone pairs have delocalization indices of around 0.0170–0.0220 in the s-trans conformers, perhaps indicative of the spread of the lone pair onto adjacent centers in the absence of any donor–acceptor interaction.

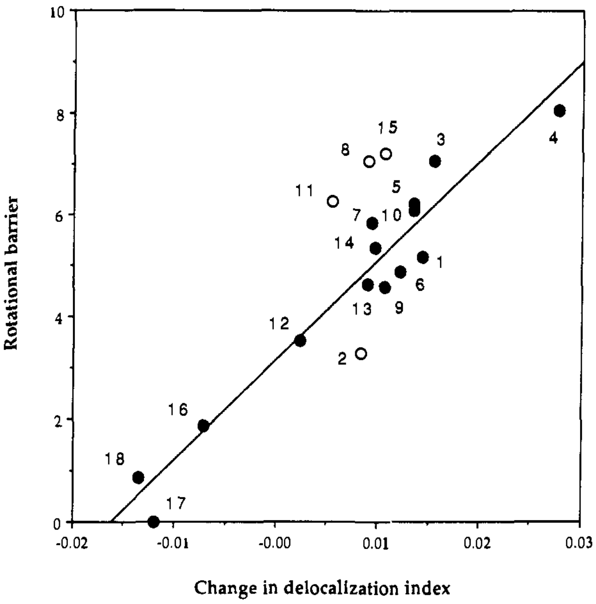

Figure 5. Relationship between the barrier heights and the change in delocalization index on going from the trans form to the rotational transition state.

If π-electron delocalization is a major contributor to the rotational barrier, there should be a relationship between the barrier height and the delocalization indices. In order to test this, we have taken the difference in the sum of the delocalization indices for the 180° and the 90° forms and have plotted the barrier heights against this quantity (Figure 5). This "delocalization difference" should provide a convenient measure of the overall change in delocalization as a molecule rotates about its central bond. Here, the dark circles represent cases in which there is no carbonyl oxygen or nitrogen lone pair repulsion in the s-cis forms, and also excludes 2-azabutadiene (**2**). It can be seen that there is a fair linear relationship between the quantities, suggesting that π-electron delocalization is a major factor.

The points that lie above the line are for (*E*)-4-azaacrolein (**8**), glyoxal (**11**), and (*E*,*E*)-1,4-diazabutadiene (**15**). Here, lone pair repulsion is important at 0°, and will contribute to the barrier height.[23] 2-Azabutadiene (**2**) is unusual in that steric repulsions are substantial in the s-trans form as well as in the s-cis form. This results from the small angle about the nitrogen atom and the bulky methylene groups which are at both ends of the molecule. The resulting increase in the energy of the 180° conformer causes the relative energy of the transition state, i.e., the barrier height, to be lower than one would predict in the absence of steric factors. Since the delocalization indices have no steric component, it is not surprising that 2-azabutadiene should have a lower barrier than predicted and thus fall below the line.

4. Bond and Atom Properties

In other studies, we have found it useful to examine the bond properties and the atom properties of a series of related compounds in order to gain more insight into the effects of changing substituents. Here, we make use of Bader's theory of atoms in molecules[22] in which the charge density distribution derived from the ab initio calculations is analyzed in terms of the molecular topology. The analysis begins with the location of the bond critical

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[23] (*E*)-*C*-nitrosomethanimine (**9**) and nitrosoformaldehyde (**12**) might also be expected to exhibit strong lone pair repulsions in the s-cis conformers. However, it appears that they do not, and this seeming discrepancy can be attributed to the special properties of the nitroso group. The calculated bond orders for the N═O bonds (section 4) are significantly greater than 2, which suggests that there is substantial triple bond character. This in turn would suggest that the oxygen atom only has one high-energy lone pair not involved in any bonding interaction, and that it would point directly away from the nitrogen atom (since it would have roughly sp hybridization). If this were indeed the case, the lone pair would not be well oriented to cause repulsions in s-cis heterobutadienes, and we should not be suprised if lone pair repulsions are small for those compounds containing nitroso groups.

Table VII. Atomic Charges[a]

Butadiene (**1**)

τ (deg)	C1	C2	H5	H6	H7	total
0	0.001	0.001	0.006	−0.001	−0.007	0.000
37.7	0.002	−0.007	0.003	0.004	−0.002	0.000
101.6	0.006	−0.017	0.001	0.003	0.008	0.000
180	−0.006	0.002	0.006	−0.002	−0.001	−0.002

2-Azabutadiene (**2**)

τ (deg)	C1	N2	C3	C4	H5	H6	H7	H8	H9	total
0	0.875	−1.410	0.468	0.004	0.030	0.007	0.020	0.015	−0.007	0.002
54.2	0.863	−1.426	0.451	0.025	0.028	0.021	0.028	0.009	0.024	0.000
111.0	0.878	−1.418	0.408	0.051	0.028	0.012	0.021	0.005	0.015	−0.001
180	0.855	−1.421	0.472	0.029	0.030	0.003	−0.007	0.007	0.033	0.001

Acrolein (**3**)

τ (deg)	C1	C2	C3	O4	H5	H6	H7	H8	total
0	0.005	−0.012	1.129	−1.240	0.030	0.073	0.009	0.009	0.002
91.4	0.039	−0.050	1.131	−1.220	0.024	0.017	0.038	0.023	0.002
180	−0.019	0.004	1.137	−1.234	0.037	0.022	0.048	0.007	0.002

Nitrosoethylene (**4**)

τ (deg)	C1	C2	N3	O4	H5	H6	H7	total
0	0.029	0.365	−0.081	−0.491	0.047	0.085	0.044	−0.002
93.8	0.095	0.289	−0.067	−0.458	0.037	0.037	0.070	0.001
180	0.021	0.430	−0.140	−0.490	0.048	0.064	0.070	0.003

(*E*)-1-Azabutadiene (**5**)

τ (deg)	N1	C2	C3	C4	H5	H6	H7	H8	H9	total
0	−1.272	0.858	−0.006	0.010	0.352	−0.007	−0.006	0.014	0.061	0.003
95.2	−1.259	0.858	−0.021	0.025	0.349	0.007	0.024	0.011	0.008	0.001
180	−1.267	0.861	0.011	−0.015	0.351	−0.003	0.041	0.021	0.004	0.004

(*Z*)-1-Azabutadiene (**6**)

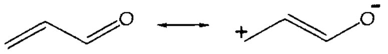
τ (deg)	N1	C2	C3	C4	H5	H6	H7	H8	H9	total
0	−1.270	0.865	−0.007	0.006	0.348	0.006	0.004	0.027	0.026	0.002
31.7	−1.250	0.862	−0.018	0.002	0.340	0.015	0.014	0.022	0.015	0.003
97.7	−1.255	0.860	−0.047	0.019	0.346	0.024	0.024	0.016	0.015	0.001
180	−1.255	0.867	−0.008	−0.002	0.337	0.013	0.008	0.025	0.017	0.001

[a] The calculations were based on RHF/6-311++G** wave functions obtained at the MP2/6-31G* geometries.

point which is the point of minimum charge density along the path joining two bonded atoms. Starting at this point, rays are developed for which the charge density decreases most rapidly. A set of such rays forms a zero-flux surface that separates the pair of atoms. A set of these surfaces serves to separate the molecule into a group of atomic domains, each of which may be treated independently.

The bond properties (charge density at the bond critical point, the components of the Laplacian of the charge density at the critical point, etc.) are available as supplementary material. The electron populations for the atoms were obtained by numerical integration of the charge density within each of the atomic domains. They were converted to atomic charges by subtracting the atomic numbers (=nuclear charge). Some representative values are summarized in Table VII, and the remaining data are available as supplementary material. As part of this analysis, one obtains an atomic overlap matrix from which bond orders may be calculated.[20] They are given in Table VIII and the supplementary material.

The change in charge density on rotation provides a way in which to examine the contribution of zwitterionic forms such as



The contribution of the zwitterionic form will disappear after a 90° rotation about the central C–C bond. The data for acrolein in Table VII show that the terminal methylene group's charge goes from +0.040 in the trans form to +0.080 at 90° and +0.108 at 0°. Thus, rather than decreasing on rotation from 180° to 90°, the charge increases. The change in charge is that expected for the interaction of the C—O dipole with the C=C bond. The negative charge on oxygen will polarize the C=C bond in the observed fashion. In accord with this proposal, the hydrogen closest to the oxygen in the s-cis form has the largest positive charge. The same type of charge shifts are found with 1-azabutadiene (**5** and **6**).

The charges given above are the sum of the σ- and π-components. In our earlier study of butadiene[2] we found an important σ/π interaction. When the π-electrons shifted in one direction, the σ-electrons shifted in the opposite direction so as to minimize electron repulsion. In order to see how the σ- and π-electrons interact in acrolein, we have calculated these components. With the cis and trans rotamers, MOs 13 and 15 are the two π-orbitals. For the 90° form, the π-values are based on the same two orbitals which are still largely the π-orbitals (one is mostly a C=O bond orbital and the other mostly a C=C bond orbital). In the trans rotamer, the terminal methylene group has σ- and π-charges of −0.105 and +0.146; at 90° they become +0.113 and −0.033; and for the cis rotamer they are −0.020 and +0.128. It can be seen that there is a shift of 0.1 π-electron in the direction expected for a contribution by the zwitterionic structure on going from the s-trans rotamer to the transition state, but there also is a shift in σ-electrons to compensate. In the s-cis rotamer, the σ-charge is similar to that in s-trans, but the π-charge has increased, corresponding to the polarization of the π-bond by the carbonyl.

The charges at the groups adjacent to the nitrogen in 2-azabutadiene (**2**) are interesting. The positive charge at the methylene group is about twice as large as that for the CH group. This might be expected based on the greater polarizability of a double bond as compared to a single bond. Again, it is possible to separate the σ- and π-components of the charge. The π-charge at C1 is +0.382, and that at C3 is +0.100, and the corresponding σ-charges

Table VIII. Covalent Bond Orders Based on RHF/6-311++G** Wave Functions at MP2/6-31G* Geometries

Butadiene (**1**)

	τ (deg)	total		π		σ	
		C—C	C=C	C—C	C=C	C—C	C=C
	0	1.0861	1.8767	0.0903	0.8410	0.9958	1.0357
min	37.7	1.0894	1.8716				
TS	101.6	1.0688	1.8910				
	180	1.1029	1.8656	0.1031	0.8330	0.9998	1.0326

2-Azabutadiene (**2**)

	τ (deg)	total			π			σ		
		C—N	C=N	C=C	C—N	C=N	C=C	C—N	C=N	C=C
	0	0.9662	1.6035	1.8398	0.1159	0.7688	0.8181	0.8503	0.8347	1.0217
min	54.2	0.9635	1.5977	1.8267						
TS	111.0	0.9568	1.6121	1.8464						
	180	0.9685	1.6051	1.8145	0.1334	0.7772	0.8023	0.8351	0.8278	1.0122

Acrolein (**3**)

	τ (deg)	total			π			σ		
		C—C	C=O	C=C	C—C	C=O	C=C	C—C	C=O	C=C
	0	1.0677	1.3634	1.8369	0.1014	0.6039	0.8055	0.9663	0.7595	1.0315
TS	91.4	1.0198	1.3967	1.8909						
	180	1.0640	1.3643	1.8423	0.1006	0.6084	0.8098	0.9635	0.7559	1.0325

Nitrosoethylene (**4**)

	τ (deg)	total			π			σ		
		C—N	N=O	C=C	C—N	N=O	C=C	C—N	N=O	C=C
	0	0.9637	2.0462	1.8031	0.1318	0.8860	0.7787	0.8319	1.1602	1.0244
TS	93.8	0.9108	2.0685	1.8569						
	180	0.9639	2.0417	1.7704	0.1552	0.8814	0.7566	0.8087	1.1603	1.0137

(*E*)-1-Azabutadiene (**5**)

	τ (deg)	total			π			σ		
		C=C	C—C	C=C	C=C	C—C	C=N	C=C	C—C	C=N
	0	1.8532	1.0614	1.6007	0.8218	0.0911	0.7589	1.0314	0.9703	0.8418
	45	1.8631	1.0507	1.6081						
	90	1.8888	1.0257	1.6245						
TS	95.2	1.8897	1.0246	1.6243						
	135	1.8706	1.0443	1.6086						
	180	1.8568	1.0598	1.5957	0.8232	0.0921	0.7575	1.0336	0.9677	0.8382

(*Z*)-1-Azabutadiene (**6**)

	τ (deg)	total			π			σ		
		C=C	C—C	C=N	C=C	C—C	C=N	C=C	C—C	C=N
	0	1.8596	1.0623	1.6019	0.8356	0.0822	0.7585	1.0240	0.9801	0.8434
min	31.7	1.8668	1.0583	1.6099						
TS	97.7	1.8896	1.0343	1.6247						
	180	1.8511	1.0696	1.5987	0.8246	0.0929	0.7576	1.0265	0.9767	0.8411

are +0.478 and +0.368. Thus, in accord with expectations, the largest difference is found in the π-charges.

The atomic charges at oxygen and nitrogen are negative whereas those at adjacent carbons are positive, in accord with the difference in electronegativity. The calculated charges may appear rather large, but it must be remembered that they are the first term of a Taylor's series expansion that includes the atomic dipoles and higher terms. The atomic dipoles arise from the fact that the center of charge does not coincide with the nuclear position. The total dipole moment is obtained by summing the charge terms and the atomic dipoles.

The covalent bond orders that are derived from the atomic overlap matrix are given in Table VIII. For butadiene, the central C–C bond has a bond order somewhat greater than 1, and the double bond has a bond order somewhat less than 2, in accord with expectations. The bond orders for the planar forms have been separated into σ- and π-components, and it can be seen that the deviations from the nominal values are found in the π-components. Futhermore, there is a small but significant decrease in the bond order of the central C–C bond upon rotation from 180° to 90° (1.09 and 1.10 in the s-cis and s-trans forms vs 1.07 in the 90° form) which is consistent with the loss of π-delocalization. The greatest change occurs in the case of nitrosoethylene (**4**) (0.96 in the planar forms vs 0.91 at 90°), which also exhibits the largest variation in delocalization indices. With 2-azabutadiene (**2**) the C=C bond order is somewhat less than that for butadiene, in accord with the changes in delocalization indices in Table VI. The C=N bond order is less than 2 because it has a significant polar component. The same is found with C=O groups, as in acrolein (**3**). The N=O bond, as in nitrosoethylene (**4**) is unique in that it has a covalent bond order greater than 2, despite having some ionic contribution. This suggests some triple bond character.

There is not a good correlation between the covalent bond orders and the energy difference between the s-trans and transition state rotamers. However, this is to be expected since the bond orders reflect only the covalent part of the bonds, and there are significant ionic components.

5. Bond Dissociation Energies

We were interested in seeing if additional information could be obtained for these compounds, and therefore we have examined the dissociation energies of the central bonds. This required calculating the energies of the radicals that would be formed. The geometries were obtained at the UMP2/6-31G* level of theory,

Table IX. Calculated Energies of Radicals

compd	HF/6-31G*	MP2/6-31G*	MP3(fc)/6-311++G**[a]	ZPE
$CH_2{=}CH$	−77.390 29	−77.613 26	−77.690 39	21.86
$CH_2{=}N$	−93.432 31	−93.678 56	−93.754 91	15.10
$O{=}CH$	−113.247 66	−113.540 33	−113.602 89	8.12
$O{=}N$	−129.247 88	−129.564 46	−129.628 42	2.86
$NH{=}CH$ (cis)	−93.392 96	−93.659 25	−93.727 72	15.23
$NH{=}CH$ (trans)	−93.398 75	−93.668 63	−93.736 48	15.62

[a] Calculated at the MP2/6-31G* geometries. Spin contamination was projected out in obtaining these energies. The 6D option was used for the d polarization functions.

Table X. Calculated Bond Dissociation Energies, MP3(fc)/6-311++G**//MP2/6-31G*[a]

compd	MP2	MP3	corr[b]	obsd (0 K)
butadiene (**1**)	127.1	108.9	113.9	115.8 ± 0.8
2-azabutadiene (**2**)	100.8	79.4	84.4	
acrolein (**3**)	102.3	90.9	95.9	98.4 ± 2.3
nitrosoethylene (**4**)	59.2	43.5	48.5	
(*E*)-1-azabutadiene (**5**)	112.8	98.7	103.7	
(*Z*)-1-azabutadiene (**6**)	117.5	102.7	107.7	
(*Z*)-4-azaacrolein (**7**)	85.3	77.8	82.8	
(*E*)-4-azaacrolein (**8**)	81.3	74.5	79.5	
(*E*)-*C*-nitrosomethanimine (**9**)	38.1	27.3	32.3	
(*Z*)-*C*-nitrosomethanimine (**10**)	45.0	33.7	38.7	
glyoxal (**11**)	70.4	66.6	71.6	70.9 ± 1.9
nitrosoformaldehyde (**12**)	29.1	21.2	26.2	
(*Z*,*Z*)-1,4-diazabutadiene (**13**)	101.5	90.4	95.4	
(*E*,*Z*)-1,4-diazabutadiene (**14**)	97.4	87.1	92.1	
(*E*,*E*)-1,4-diazabutadiene (**15**)	93.1	83.3	88.3	
methyleneformamide (**16**)	80.1	65.0	70.0	
2,3-diazabutadiene (**17**)	65.3	41.4	46.4	
N-nitrosomethanimine (**18**)	29.6	11.9	16.9	

[a] The energies (kcal/mol) are corrected for the zero-point energy changes. [b] Including a higher level correction of 5.0 kcal/mol.

and the energies were calculated at these geometries using UMP3/6-311++G**. The energies given in Table IX were corrected for the small spin contamination found in the calculations. The dissociation energies derived from these data followed by correction for the changes in zero-point energies are given in Table X. Pople has shown in his G1 scheme that improved estimates of dissociation energies may be obtained by including higher level corrections derived from the differences between the calculated and observed energies of the hydrogen molecule and of the hydrogen atom.[24] With the present data, the higher level correction is 5.0 kcal/mol, and when applied to the MP3 calculated values it gives the energies recorded as corrected in Table X.

The heats of formation at 0 K are known for the vinyl and formyl radicals. This allows the calculation of the bond dissociation energies of butadiene (**1**), acrolein (**3**), and glyoxal (**11**), and they are also given in Table X. The calculated energy changes are in rather good agreement with experiment, and therefore it is reasonable to assume that all of the calculated dissociation energies provide useful estimates of the correct values.

The high bond dissociation energy for butadiene (**1**) must result mainly from the hybridization. The central bond will be formed using sp^2 hybrid orbitals, and it is well established that bonds become stronger as the % s-character increases. The very low BDE of *N*-nitrosomethanimine (**18**) makes it unlikely that it will be formed under ordinary reaction conditions. All of the compounds that would decompose to give NO as one of the fragments have low BDE values at least in part because of the unusual stability of the NO radical.

The formyl radical also is relatively stable: the bond dissociation energy for acetaldehyde is 5 kcal/mol less than that for ethane. Correspondingly, all of the compounds having a carbonyl group (**3**, **7**, **8**, **11**, **12**, and **16**) have relatively low BDE values as compared to butadiene.

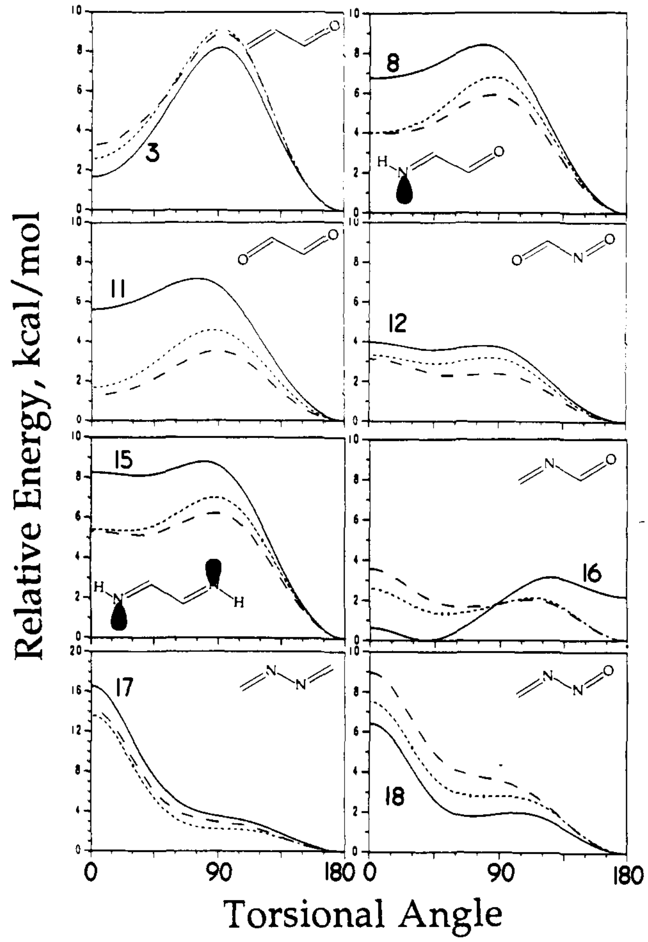


Figure 6. Effect of a polar medium on the rotational profiles. The solid line gives the HF/6-31G* relative energies for $\epsilon = 1$, the short dashes give the HF/6-31G* energies for $\epsilon = 80$, and the long dashes give the HF/6-311++G** energies for $\epsilon = 80$.

6. Solvent Effects

The data in Table I show that there are significant changes in dipole moment on rotation about the central bonds. As a result, the ground and transition states will be differentially affected by solvents, and the rotational profiles may be significantly different in solution. We have shown that Onsager's reaction field model,[25] as incorporated into ab initio molecular orbital theory, is quite successful in reproducing the solvent effects for a number of equilibria.[26] Therefore, we have employed this model in studying the solvent effect on heterobutadienes. The dielectric constant was taken as 80, corresponding to a relatively high value, and the cavity radius, a_0, was obtained from the calculated molecular volume, and an empirically determined correction of 0.5 Å was added. The a_0 values and the calculated energies are given in Table XI.[27] Data for additional torsional angles are given in the supplementary material. The rotational profiles calculated for the gas phase are compared with the solution values in Figure 6. Here, the HF/6-31G* relative energies for the gas phase are shown as solid lines, and the HF/6-31G* energies for a medium with

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(27) The a_0 values for acrolein and glyoxal were computed from the experimental densities in the liquid phase. For comparison, these a_0 values were also computed from the calculated molecular volumes in the same way as for all the other compounds. For acrolein, the two methods give almost identical results: $a_0 = 3.51$ from the calculated molecular volume vs $a_0 = 3.48$ from the experimental density. For glyoxal the two methods differ somewhat more, but are still in reasonable agreement: $a_0 = 3.34$ from the calculated molecular volume vs $a_0 = 3.22$ from the experimental density. These discrepancies in the numerical values of a_0 are too small to cause significant changes in the SCRF torsional potential.

Table XI. SCRF Calculated Energies of Heterobutadienes in a Medium with ϵ = 80.0[a]

	τ (deg)	6-31G* (hartrees)	*E*(rel) (kcal/mol)	6-311++G** (hartrees)	*E*(rel) (kcal/mol)
Acrolein (**3**)					
	0	−190.76240	2.59	−190.81630	3.26
a_0 = 3.48 TS	91.5	−190.75199	9.12	−190.80728	8.91
	180	−190.76652	0.00	−190.82149	0.00
(*E*)-4-Azaacrolein (**8**)					
	0	−206.75376	4.00	−206.81538	3.97
a_0 = 3.42 TS	89.7	−206.74938	3.84	−206.81232	5.89
	180	−206.76014	0.00	−206.82171	0.00
Glyoxal (**11**)					
	0	−226.58950	1.68	−226.65645	1.29
a_0 = 3.22 TS	86.6	−226.58486	4.59	−226.65287	3.53
	180	−226.59218	0.00	−226.65850	0.00
Nitrosoformaldehyde (**12**)					
	0	−242.50531	3.34	−242.57630	3.14
a_0 = 3.26 min	44.8	−242.50600	2.91	−242.57748	2.40
TS	82.7	−242.50551	3.21	−242.57747	2.40
	180	−242.51063	0.00	−242.58130	0.00
(*E*,*E*)-1,4-Diazabutadiene (**15**)					
	0	−186.91138	5.42	−186.96835	5.33
a_0 = 3.50 min	13.3	−186.91146	5.37	−186.96899	4.93
	180	−186.92001	0.00	−186.97685	0.00
Methyleneformamide (**16**)					
	0	−206.76130	2.60	−206.81930	3.59
a_0 = 3.42 min	52.8	−206.76332	1.34	−206.82216	1.79
TS	114.2	−206.76206	2.13	−206.82178	2.03
	180	−206.76545	0.00	−206.82502	0.00
2,3-Diazabutadiene (**17**)					
	0	−186.86424	13.65	−186.91482	14.24
a_0 = 3.50 min	45	−186.87744	5.37	−186.92771	6.15
	180	−186.88600	0.00	−186.93751	0.00
N-Nitrosomethanimine (**18**)					
	0	−222.65322	7.52	−222.71570	8.98
a_0 = 3.36 min	73.8	−222.66072	2.81	−222.72403	3.75
TS	98.8	−222.66074	2.80	−222.72458	3.41
	180	−222.66520	0.00	−222.73001	0.00

[a] All SCRF energies were obtained at the SCRF HF/6-31G* optimized geometries.

Table XII. XCRF Calculated Atomic Charges Based on RHF/6-311++G**//RHF/6-31G* Wave Functions

Acrolein (**3**)

τ (deg)	C1	C2	C3	O4	H5	H6	H7	H8	total
0	0.021	0.000	1.188	−1.289	0.038	0.041	0.017	−0.013	0.003
91.5	0.073	−0.058	1.191	−1.275	0.032	0.005	0.028	0.005	0.002
180	0.012	0.005	1.184	−1.297	0.055	0.031	0.022	−0.010	0.002

Glyoxal (**11**)

τ (deg)	C1	O3	H5	total	τ (deg)	C1	O3	H5	total
0	1.179	−1.224	0.045	−0.001	180	1.185	−1.225	0.042	0.003
86.6	1.196	−1.243	0.047	0.001					

a dielectric constant of 80 are given by the short dashed lines and the HF/6-311++G** energies for ϵ = 80 are given by the long dashed lines.

With acrolein (**3**), the barrier is calculated to increase slightly on going from the gas phase to a polar medium. This has also been found by and Katritzky and Karelson via semiempirical SCRF calculations, and they have suggested that it indicates the importance of dipolar resonance structures in the ground state of the molecule.[28] In order to examine the effect of solvent on the charge distribution, we have examined the atomic charges for solvated acrolein (Table XII). The polarization of the carbonyl group was found to increase slightly, as might be expected. However, the charge at the methylene group is now essentially invariant to rotation (+0.098 for trans, +0.110 at 90°, and +0.100 for cis). Thus, the polarization of the C═C bond by the carbonyl is markedly reduced on going from the gas phase to a polar medium. The delocalization indices are only slightly changed on going from ϵ = 1 to ϵ = 80 (Table XIII). It is likely that there are some shifts in σ- and π-electron populations on rotation about the central C–C bond, as was found for the gas phase, but the net effect is neglible.

Larger changes were found with the torsional profiles of **8**, **11**, **15**, and **16**, and as might be expected, these are the cases in which the largest changes in dipole moment occur on rotation about the central bond. With glyoxal (**11**) and (*E*,*E*)-1,4-diazabutadiene (**15**) the dipole moment is 0 for the s-trans form and increases to 3.8 and 3.3 D, respectively, at the torsional transition state. With (*E*)-4-azaacrolein (**8**) it increases from 2.7 to 4.2 D on going from the trans form to the transition state. Quite different behavior is found with methyleneformamide (**16**). Here, the dipole moment is largest (5.3 D) for the s-trans form and it decreases

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

Table XIII. Results of Boys Localizations with $\epsilon = 80$[a]

bonds	τ (deg)	deloc index		
		Acrolein (**3**)		
		C=O	C=C	
$\sigma + \pi$	0	0.0077	0.0309	
$\sigma + \pi$	90	0.0069	0.0180	
$\sigma + \pi$	180	0.0081	0.0336	
π	0	0.0126	0.0552	
π	180	0.0134	0.0607	
		Nitrosoformaldehyde (**12**)		
		C=O	N=O	LP on N
$\sigma + \pi$	0	0.0119	0.0088	0.0156
$\sigma + \pi$	90	0.0118	0.0075	0.0202
$\sigma + \pi$	180	0.0138	0.0099	0.0176
π	0	0.0193	0.0143	
π	180	0.0231	0.0165	
		Methyleneformamide (**16**)		
		C=O	C=N	LP on N
$\sigma + \pi$	0	0.0125	0.0244	0.0179
$\sigma + \pi$	90	0.0137	0.0142	0.0410
$\sigma + \pi$	180	0.0140	0.0259	0.0202
π	0	0.0194	0.0428	
π	180	0.0221	0.0462	

[a] The calculations were based on RHF/6-311++G** wave functions at the RHF/6-31G* geometries.

to 3.0 D for the minimum energy gauche form and 2.0 D for the s-cis form.

7. Conclusion

The difference in energy between the s-cis and s-trans rotamers is a result of several factors: steric interactions between the hydrogens of terminal CH_2 or NH groups in the s-cis rotamers; lone pair–lone pair repulsive interactions; and dipole–dipole repulsion.

The barrier to rotation is in considerable measure a result of the loss of π-electron delocalization on going from the s-trans rotamer to the transition state. This is seen in the correlation of the change in delocalization index with the barrier height. The delocalization index correlates with common expectations concerning the polarizability of double bonds. Thus, a C=C is best able to delocalize its π-electrons into adjacent double bonds, and the ability decreases in the order C=C > N=C > C=N > C=O. The ability to accept π-electrons takes the opposite order: N=O > N=C > C=O > C=N > C=C.

However, the conventional view of delocalization is not complete. This is well illustrated by acrolein, where the zwitterionic form is commonly considered to contribute to the ground-state structure. The above analysis found that the total charge at the terminal methylene group becomes more positive on going from s-trans to the transition state, contrary to the prediction of the conventional zwitterionic hypothesis. Rotation to the s-cis form further increased the positive charge showing that the dominant factor was the interaction of the carbonyl dipole with the polarizable C=C bond. This was further shown by an examination of the effect of a dipolar medium which should minimize such interactions. Here, the charge at the terminal methylene was essentially invariant to rotation about the central C–C bond.

The zwitterionic structure does contribute to the π-bonding in acrolein as seen by the changes in the π-charges on rotation. However, the σ-electrons compensate for the changes in π-populations, leading to a net charge that does not reflect the contribution of the zwitterionic structure.

On the basis of this and other studies in this series,[2,29] we can make the following observations for butadiene and the heterobutadienes, which appear to be quite general: (1) π-delocalization effects have the energetic consequences generally expected, (2) π-delocalization does *not* generally affect charge distributions in the commonly predicted manner, since the σ-electrons tend to counteract any movement by the π-electrons, and (3) dipolar, lone pair–lone pair, and steric interactions influence the energy essentially independently of π-delocalization effects. Finally, we might point out that lone pair–lone pair repulsions are often the strongest of these interactions.

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Supplementary Material Available: Listing of calculated energies, structural data in Z matrix format, bond and atom properties of the compounds in this report, and torsional profiles for several fluorinated and methylated butadienes (see footnote 17) (92 pages). Ordering information is given on any current masthead page.

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(29) Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.*, submitted for publication.