Table 1 Angles between vector $\nabla(\Delta q(\xi))$ and momentum vectors corresponding to the vibrational normal modes of the C_{2v} stationary point for radical ion **1**.

Normal Mode (Symmetry)	Angle	Normal Mode (Symmetry)	Angle	Normal Mode (Symmetry)	Angle
1 (A_2)	89.7	36 (A_2)	89.8	71 (B_2)	84.9
2 (A_1)	89.9	37 (B_1)	89.6	72 (A_1)	89.8
3 (B_1)	89.9	38 (A_1)	89.6	73 (A_2)	90.0
4 (B_1)	89.7	39 (B_2)	83.2	74 (B_1)	89.5
5 (B_2)	88.6	40 (B_1)	89.5	75 (A_1)	88.9
6 (A_2)	89.7	41 (A_2)	89.2	76 (B_2)	88.1
7 (A_1)	89.4	42 (B_1)	89.0	77 (B_1)	89.0
8 (A_2)	89.8	43 (A_2)	89.5	78 (A_2)	89.9
9 (B_1)	89.8	44 (B_1)	88.9	79 (A_1)	90.0
10 (A_1)	89.7	45 (A_1)	89.7	80 (B_1)	89.8
11 (B_2)	85.2	46 (B_2)	89.8	81 (A_1)	89.8
12 (B_2)	89.3	47 (A_1)	89.8	82 (B_2)	84.4
13 (A_1)	89.4	48 (B_2)	84.9	83 (A_1)	89.9
14 (A_2)	89.9	49 (A_1)	89.7	**84 (B_2)**	**13.6**
15 (B_1)	89.3	50 (A_2)	89.9	85 (A_1)	89.9
16 (B_2)	85.4	51 (B_2)	88.0	86 (A_2)	90.0
17 (A_2)	89.6	52 (B_1)	89.9	87 (B_1)	89.9
18 (B_2)	87.3	53 (A_2)	90.0	88 (B_2)	89.1
19 (A_1)	89.8	54 (B_2)	86.3	89 (A_1)	89.9
20 (B_1)	89.8	55 (A_1)	89.8	90 (B_2)	87.5
21 (A_2)	90.0	56 (B_1)	89.4	91 (A_1)	89.8
22 (B_1)	89.9	57 (A_1)	89.8	92 (B_2)	88.6
23 (A_1)	90.0	58 (B_1)	88.4	93 (B_1)	89.8
24 (B_2)	84.2	59 (A_2)	88.9	94 (A_1)	90.0
25 (A_1)	89.6	60 (B_2)	79.4	95 (A_2)	89.8
26 (A_2)	89.9	61 (A_1)	89.6	96 (B_1)	89.9
27 (B_1)	89.6	62 (A_2)	90.0	97 (B_2)	89.8
28 (A_2)	89.7	63 (B_1)	89.8	98 (A_1)	89.9
29 (B_1)	89.5	64 (B_2)	87.4	99 (A_1)	90.0
30 (B_2)	86.8	65 (A_2)	89.5	100 (B_2)	87.3
31 (A_1)	89.9	66 (B_1)	89.6	101 (A_1)	89.8
32 (B_2)	85.6	67 (A_2)	89.3	102 (A_2)	89.6
33 (B_2)	80.1	68 (B_1)	88.9	103 (B_1)	89.6
34 (A_2)	89.2	69 (A_1)	89.4	104 (B_2)	72.5
35 (A_1)	89.8	70 (B_2)	89.4	105 (A_1)	89.4

Comparison of Semiempirical and Ab Initio Results

The AM1 calculations were carried out with the MOPAC93 package.[1] All stationary points were optimized to a gradient norm <0.1. Harmonic vibrational frequency calculations were carried out on all stationary points in order to differentiate minima from transition structures and higher order stationary points. Ab initio UHF and UB3LYP calculations were carried out with the Gaussian 94 package.[2] Results of the ab initio calculations are summarized and compared with those from the semiempirical calculations in Table 2.

The original intention of comparing the AM1 and ab initio calculations was to find out how well the results from the approximate semiempirical procedure reflected those from the nominally more rigorous techniques. In the event, the results highlighted how difficult it is to do even reasonably high-level ab initio calculations on radical cations of the kind considered in the present work. As the results in Table 2 show, the UHF calculations afforded what seem to be unreasonably large energy differences between C_{2v} and C_s geometries. Very probably this is a result of doublet instability, which could be expected to destablilize the more symmetrical structure. Indeed, a stability calculation[3] on the UHF/3-21G $^2B_2$ wavefunction for the C_{2v} cation radical **1** revealed that it is unstable with respect to distortion to $^2A'$ symmetry. This results in charge localization at one of the double bonds. The resulting optimized $^2A'$ "localized" wavefunction is calculated to be 14.7 kcal/mol more stable than the $^2B_2$ "delocalized" wavefunction. In contrast,

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but not unexpectedly, the UHF $^2A'$ wavefunction for the C_s cation radical **1** is stable. Curiously, the hybrid HF/DFT procedure UB3LYP apparently erred in the other direction, making the C_{2v} structure the global minimum for radical ions **1** and **2**. While it is possible that the coupling in **1** is sufficiently strong for this molecule to possess a delocalized C_{2v} ground state structure, this is unlikely to be the case for **2**. The sizes of the molecules preclude use of more sophisticated post-HF techniques, at least with a basis set of any reasonable size, and so the net result is that the original goal of using the ab initio calculations to calibrate the semiempirical ones could not be accomplished.

At the UB3LYP/3-21G level, the C_{2v} $^2B_2$ state of **4** is a minimum, however, only 3.2 kcal/mol higher is a $^2A_1$ state that is unstable with respect to cleavage of the C3-C10 bond.   It is quite likely that the ring opening seen in the semiempirical molecular dynamics results from mixing of these two states in structures of low symmetry.

Overall, the results from the semiempirical calculations were more in accord with general expectations for the properties of the radical cations **1** to **4** than were those from any of the ab initio methods.   It is quite possible that this is a result of the use of the half-electron model in the AM1 calculations. This has previously been shown to be an operationally useful way of dealing with the doublet instability problem.[4]

Table 2

	C_s symmetry		C_{2v} symmetry		
Method	E (hartree)	N(i)[a]	E (hartree)	N(i)[a]	E_{rel} (kcal/mol)[b]
Radical ion **1**					
AM1 2 X 2 CI		0		0	1.38
UHF/3-21G	-651.4334837	0	-651.4040125	0	18.49
UHF/6-31G(d)	-655.0436463		-655.0109798	0	20.50
UB3LYP/6-31G(d)	c		-659.4687214	0	
Radical ion **2**					
AM1 2 X 2 CI		0		0	2.56
UHF/3-21G	-843.1983741	0	-843.1639279	0	21.62
UHF/6-31G(d)			-847.8278555	0	
UB3LYP/3-21G	c		-848.9991822	0	
Radical ion **3**					
AM1 2 X 2 CI		0		1	3.14
UHF/3-21G			-1034.927080	0	
UB3LYP/3-21G			-1042.090535	0	
Radical ion **4**					
AM1 2 X 2 CI		0		1	2.03

[a] Number of imaginary vibrational frequencies.

[b] Energy difference between C_{2v} and C_s structures (without ZPE correction).

[c] Not a minimum at this level of theory.

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