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THEORETICAL ANALYSIS OF THE ENERGY BARRIERS FOR THE ROTATIONAL ISOMERIZATION OF THE ALLYL AND THE 1-CYANO-, 1-HYDROXY- AND 1-CYANO-1-HYDROXYALLYL RADICALS†

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An *ab initio* computational study was carried out on the ground- and transition-state structures for the rotational isomerization of the allyl and the 1-cyano, 1-hydroxy- and 1-cyano-1-hydroxyallyl radical systems in an attempt to gain an understanding of the factors affecting the relative energy barriers for rotational isomerization. The results of ESR rate measurements have indicated that there exists the presence of an 'extra' lowering of the energy barrier for the rotational isomerization of the 1-cyano-1-hydroxylallyl radical relative to the sum of the lowerings of the energy barriers for the rotational isomerization of the 1-cyano- and 1-methoxylallyl radical compared with the energy barrier for the rotational isomerization of the allyl radical. The 'extra' lowering of the energy barrier for the rotational isomerization of the 1-cyano-1-hydroxyallyl radical has been attributed to captodative stabilization of the transition structure for rotational isomerization. Prior calculational studies in the author's and other laboratories have resulted in the suggestion that captodative substitution does not always lead to 'extra' stabilization to a radical center. Recent calculations in the author's laboratories and the results reported in the present paper strongly suggest that ground-state effects can be dominant in determining the rate of a radical-forming reaction. The present paper describes the results of theoretical calculations on the allyl and substituted allyl radical systems that indicate that ground-state effects appear to dominate the relative rates of the rotational isomerization of the substituted allyl radicals. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Numerous experimental and theoretical studies in many laboratories have focused on how various substituents interact with a radical center to affect the relative stability and reactivity of mono- and disubstituted radicals. As thermodynamic stabilization energies of substituted radicals are very difficult to obtain experimentally, theoretical approaches have proven to be very useful. (The references are too numerous to cite in this paper. For a reasonably comprehensive review on substituent effects on the relative stability and reactivity of monosubstituted radicals, and for a review of the experimental and theoretical approaches to the determination of the relative stabilities of monosubstituted radicals, see Ref. 1.). Initial theoretical calculations in the author's laboratories starting in 1984 were carried out at the *ab initio* 4–31G level of theory on the isodesmic reaction shown in equation (1). (The 4–31G level of theory employed in the early studies initiated in 1984 and reported in Ref. 1 and later in Ref. 2, was dictated by the large number of systems studied, and the computing power then available. Even with the use of that level of theory, very good correspondence was obtained between the theoretically calculated and experimentally determined values for functional group stabilization energies, as reported in Ref. 3.) The results of those calculations indicated that practically all substituents are capable of stabilizing a radical center except extremely powerful electron-withdrawing groups such as F_3C—, H_3N^+, H_2S^+ and H_3P^+.[1] Radical stabilization energies (RSEs) were defined as the overall change in total energy in going from the reactants to the products in equation (1).

$$X—\dot{C}H_2 → CH_4 → X—CH_3 + \dot{C}H_3 \qquad (1)$$

The effect of two substituents on the relative stability of a radical center has been the center of considerable controversy. Arguments have been made that the presence of an electron *donor* and an electron *acceptor* directly

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† This work is dedicated to Professor Frederick G. Bordwell in recognition of his many contributions in the area of physical organic chemistry.

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attached to a radical center should provide an 'extra stabilization' to the radical system relative to the sum of the relative stabilizations provided by the individual substituents to a similar radical center. This concept has been termed 'merostabilization,' or recently more commonly referred to as 'captodative' stabilization. (For reviews on the effect of captodative substitution on the stability of a radical center, and also the effect of captodative substitution in many other types of reactions, see Refs. 4 and 5.) Leroy and co-workers[6] were the first to study extensively the relative effects of two substituents on the relative stability of a radical center. In order to evaluate the effect of a substituent(s) on the stabilization of a radical center they employed the relationship shown in equation (2) in which $SE°$ is the stabilization energy, $\Delta H°_a$ is the heat of atomization of the non-radical species and $\Sigma N_{ab}E°_{ab}$ is the sum of the bond energy terms in the radical. This procedure depends heavily on the availability and reliability of the values for the heats of formation and bond energies. Leroy and co-workers[6] used this isodesmic relationship shown in equation (3), employing a combination of *ab initio* calculational results and experimental data to derive $SE°$ values. No consistent behaviour was observed among the 'captodative' substituted radicals; some combinations resulting in net extra stabilization, while some other combinations resulted in net destabilization.

$$SE° = \Delta H°_a - \Sigma N_{ab}E°_{ab} \qquad (2)$$

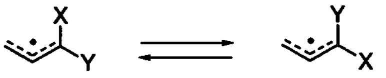
$$\mathrm{D{-}CH^{\bullet}{-}A + CH_3^{\bullet} \rightarrow D{-}CH_2^{\bullet} + {}^{\bullet}CH_2{-}A} \qquad (3)$$

In a subsequent calculational study carried out at the UHF/4–31G level of theory on the aminoboryl- and aminocyanomethyl radicals by Crans *et al.*[7] it was concluded that 'simultaneous stabilization by pi-donor and pi-acceptor substituents is significantly greater than the additive substituent stabilization energies of the individual groups.'

The results of a computational study carried out in the author's laboratories on a large number of variously disubstituted methyl radicals were used to calculate the RSEs of the disubstituted methyl radicals using the isodesmic relationship shown in equation (4).[7] The primary objective of that study was to evaluate further the possible validity of the proposed *captodative effect*. The results of the author's calculations indicated that the concept of the captodative effect is *not* universally valid.[2] Some combinations of acceptor and donor groups do result in substantial *enhanced stabilization*, e.g. the hydroxy–boryl and the amino–boryl functional group combinations.[2] However, some combinations of acceptor and donor groups result in *net destabilization*, e.g. the hydroxy- (or methoxy)–cyano combination of functional groups,[2] which that has been implied to provide captodative stabilization.[8,9] Furthermore, some combinations of acceptor–acceptor disubstituted methyl radicals are calculated to enjoy *net extra stabilization*, e.g. the cyano–cyano combination of functional groups.[2] Subsequent measurements of the oxidation potentials of substituted fluorenyl and acetophenone anions by Bordwell and Lynch[3] gave experimental radical stabilization energies which were in very good agreement with the theoretical values calculated in this author's laboratories, the results of which obtained by Bordwell and Lynch[2] were interpreted in terms of an absence of a captodative, or a *synergistic*, effect.

$$\mathrm{X{-}CH^{\bullet}{-}Y + CH_4 \rightarrow X{-}CH_2{-}Y + \dot{C}H_3} \qquad (4)$$

One combination of acceptor–donor functional group substitution that is calculated to result in net destabilization of a radical center is that of the cyano–hydroxy (methoxy) groups, a combination of functional groups that has been inferred to lend captodative stabilization to a radical center in several systems.[8,9] One such system involves the interpretation of the relative magnitudes of the energy barriers for the rotational isomerization of the 1-deuterio[10] and the 1-cyano-, 1-methoxy- and 1-cyano-1-methoxyallyl radicals determined by variable-temperature ESR measurements.[11,12] The experimental data are given in Scheme 1. The presence of the 1-cyano group lowers the energy barrier for rotational isomerization of the *anti*- to the *syn*-stereoisomer (X = CN, Y = H in Scheme 1) by 5·9 kcal/mol^{-1} (1 kcal = 4·184 kJ), while the energy barrier for the isomerization of the *syn*-steroisomer is lowered by 5·1 kcal mol^{-1}. The *anti*-1-methoxy group lowers the energy barrier for rotational isomerization by 1·4 kcal-mol^{-1}, while that for the *syn*-steroisomer is slightly lower, being 1·0 kcal mol^{-1}. The presence of both the 1-cyano and 1-methoxy functional groups results in a lowering of the energy barrier for the rotational isomerization of the *anti*-cyano stereoisomer by 9·6 kcal mol^{+1}, which represents an extra lowering of the energy barrier by 3·4 kcal mol^{-1} relative to the sum of the energy barriers for rotational isomerization of the corresponding 1-cyano-and 1-methoxy-allyl radicals; the 'extra' lowering of the energy barrier of the rotational isomerization of the *syn*-cyano stereoisomer is 3·5 kcal mol^{-1}.[2] The 'extra' lowering of the energy barrier for the rotational isomerization of the 1-cyano-1-methoxy-allyl radical relative to the sum of the lowerings in the energy barriers for the rotational isomerization of the corresponding monosubstituted allyl radicals has been attributed to *captodative stabilization* of the transition



	Y, *anti→syn*	Y, *syn→anti*
X=D, Y=H	15.7 ± 1.0	15.7 ± 1.0
X=H, Y=CN	9.8 ± 1.0	10.6 ± 1.3
X=H, Y=OMe	14.3 ± 1.5	14.7 ± 1.5
X=CN, Y=OMe	6.0 ± 0.4	6.1 ± 0.6

Scheme 1

structure(s) for the rotational isomerization of the 1-cyano-1-methoxylallyl radicals.[11,12]

This interrpetation of the ‘extra’ lowering of the barriers for rotational isomerization of the *anti*- and *syn*-1-cyano-1-methoxyallyl radicals, however, is flawed by the fact that only substituent effects on the relative energies of the transition structures for rotational isomerization were considered. What was not taken into consideration is effects the substituents might have on the relative energies of the ground-state substituted allyl radical reactants, which might have a significant, or dominant, effect on the relative energy barriers for the related rotational isomerization processes.

That ground-state substituent effects might play a dominant role on the reactivity of a particular system has been explored in the author’s laboratories. Theoretical calculations carried out at the HF/4–31G level (for basis set consistency with the calculations carried out much earlier in the author’s laboratories) on the isodesmic reaction shown in equation (5) have shown that when X and Y in structure **1** are a pair donor groups, the 1,1-disubstituted ethene may enjoy ground-state stabilization or suffer ground-state destabilization.[13] When both X and Y are a pair of acceptor and donor groups, or when both are acceptor groups, the 1,1-disubstituted ethene suffers significant ground-state destabilization.[13] For consideration in later discussions, selected results of that calculational study are summarized in Table 1. It is important to note that the 1-cyano–1-hydroxy combination of functional groups results in significant ground-state destabilization.

$$H_2C=CXY+H_2C=CH_2 \rightarrow H_2C=CHX+H_2C=CHY \quad (5)$$

In the present paper, the results of extensive, high-level UHF and post-HF calculations on the allyl radical and on the stereoisomers of the 1-cyano, 1-hydroxy- and 1-cyano-1-hydroxylallyl radicals and the transition structures for rotational isomerization of those substituted radical systems are described.

Table 1. Total energy changes (UHF/4–31G) for the isodesmic reactions for the disproportionation reactions of the 1,1-disubstituted ethenes illustrated in equation (3)

X	Y	E_a (kcal/mol^{-1})[a]
Acceptor–donor systems:		
H_2N—	H_2B—	−1·29
HO—	N≡	−6·39
H_2N—	N≡C—	−3·39
HO—	HCO—	−1·56
H_2N—	HCO—	−2·53
Acceptor–acceptor systems:		
H_2B—	H_2B—	−2·567
H_2—	N≡C—	+0·06
N≡C—	N≡C—	−8·45
Donor–donor systems:		
H_2N—	HO—	+0·43
HO—	HO—	+6·85
HO—	HS—	−3·56

[a] Negative values indicate net *destabilization* induced by the 1,1-groups relative to that in ethene and the monosubstituted ethenes.

CALCULATIONAL METHODS

The results of a recent calculational study carried out in the author’s laboratories using various calculational methods including UHF, UMP2, MCSCF and employing many different split-level basis sets, including diffuse and polarization functions, on the oriranylmethyl–allyloxy–vinyloxymethyl[14] and other similarly related systems,[15] have indicated that geometry optimization calculations carried out at the UHF/6–31G★ level of theory followed by a single-point calculation at the QCISD(T)/6–31G★ level provides differences in ground-state and reaction energy barriers that compare very favourably with known experimental values. The use of this approach gives a calculated energy barrier for the rotational isomerization of the allyl radical of 15·0 kcal mol^{-1} compared with the experimentally observed value of 15·7 ± 1·0 kcal mol^{-1} for the 1-deuterioallyl radical.[10] The use of much larger basis sets does not markedly improve the comparison of the theoretically calculated energy barriers with the experimental data. In the present study, calculations were carried out on the allyl and on the 1-hydroxyallyl radical system at a number of different split-level basis sets for comparison purposes, with single-point calculations then being carried out at the QCISD(T)/6-31G★//UHF/6–31G★ level of theory. The calculations were carried out using the Gaussian 94 suite of programs.[16] Calculations on the 1-cyano- and the 1-cyano-1-hydroxyallyl radical systems were carried out only at the geometry-optimized UHF/6–31G★ level of theory, followed by single-point calculations then being carried out at the QCISD(T)/6–31G★//UHF/6–31G★ level of theory.

RESULTS AND DISCUSSION

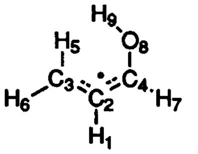
The allyl radical system

The allyl radical has been extensively studied theoretically.[17] In the present study, theoretical calculations were carried out on the allyl radical and on the transition structure for rotational isomerization of the allyl radical at a number of many different split-level basis sets, including polarization functions, the results of which are given later in Table 5. The interpretation of our results on the origin of the C_{2v} structure of the allyl radical and the origin of contributions to the energy barrier for the rotational isomerization of the allyl radical correspond with the interpretations of prior theoretical studies on the allyl radical reported in the literature.[17] The energy barrier calculated for the rotational isomerization of the allyl radical at the QCISD(T)/6–31G★/ /UHF/6–31G★ level of theory of 15·0 kcal mol^{-1} compares very favorably with the experimentally reported value of 15·7 ± 1·0 kcal mol^{-1}.

The 1-hydroxylallyl radical system

Initial optimization calculations on the four stereoisomers of the 1-hydroxylallyl radical **2ss, 2as, 2sa** and **2aa** were carried out at the UHF/6–31G★ level of theory followed by single-point calculations at the QCISD(T)/6–31G★ level of theory. [The stereochemical designation indicated by aa, as, sa and ss specify *anti–anti* (the first *anti* about the allyloxy system, the second *anti* about the allylhydroxy-OH), *anti, syn, syn, anti* and *syn, syn* conformations, respectively, of the 1-hydroxyallyl radical.] The total and relative energies are given in Table 2 and the calculated structural parameters in Table 3. *All* of the structures are essentially planar (see the calculated H_1—C_2—C_4—O_8 and C_2—C_4—O_8—H_9 dihedral angles given in Table 3), and possess five π-electron systems.

Surprisingly, the *syn*-oxyallyl (**2ss** and **2sa**) and *syn*-OH (**2ss** and **2as**) are lower in energy than their *anti* counterparts **2as** and **2aa**. An analysis of the π and σ interactions, as indicated by the respective Mulliken populations (MPs) between C_3 and O_8, H_9 and C_2, and H_1 and H_9, provides a very reasonable explanation for this calculated trend in relative stabilities (see Table 4). The SOMO of the 1-hydroxylallyl radical is a $\boldsymbol{\psi}_3$ buta-1,3-diene-type π MO which is 1,4-bonding, as is illustrated in the MO representation **3**. The MP contribution of this interaction apparently results in the *syn*-allyloxy conformation being favored over the *anti*-conformation. As C_3 and O_8 are much closer in **2ss** and **2sa** than in **2as** and **2aa**, the attractive π MPs are significantly greater in magnitude than in the *syn*-oxyallyl system compared with the *anti*-oxallyl systems. The $\sigma(C_3–O_8)$ MPs in **2ss**, however, are more repulsive than in **2sa**, but the σ(Hg–C_2) MPs are significantly more attractive in **2ss** than in **2sa**. Overall, the sum of the π and σ MPs favors **2ss** over **2sa** and, in a similar fashion, **2as** over **2aa**. (It must be recognized that the use of summed MPs from split-valence level calculations can be criticized, but it must also be recognized that the MPs do represent bonding interactions as being the product of $c_ic_jS_{ij}$.)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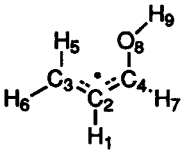
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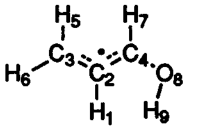
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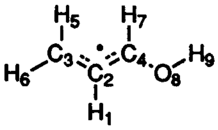
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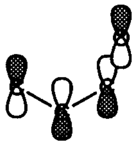

3 (SOMO)

Recognizing that the conformations of the 1-methoxyallyl radical corresponding to **2ss** and **2as** should not be lower in energy than those corresponding to their **2sa** and **2aa** counterparts because of the much larger 'size' of the methyl group relative to the hydrogen atom, further calculations were carried out on only the stereoisomers **2sa** and **2aa** with larger basis sets. The total energies are given

Table 2 Total and relative energies and $<S>$ values for the 1-hydroxylallyl radicals and transition structures for rotational isomerization

Method basis set	**2ss**	**2sa**	**2as**	**2aa**	**4s**	**4a**
UHF/6–31G★	− 191·32046 (0.00) <0·95>	− 191·31999 (0.29) <0·96>	− 191·32026 (0·13) <0·95>	− 191·31936 (0·69) <0·96>	− 191·29229 (17·7) <0.80>	− 191·29023 (19·0) <0·82>
QCISD(T)/6–31G★	− 191·90770 (0·00)	− 191·90537 (1·02)	− 191·90606 (0·59)	− 191·90461 (1·51)	− 191·88325 (14·9)	− 191·88102 (16·3)
UHF/6–31 + G★		− 191·32804 (0·00) <0·95>		− 191·32733 (0·69) <0·96>		− 191·23932 (18·9) <0·80>
UHF/6–31 + + G★		− 191·32858 (0·00) <0·95>		− 191·32750 (0·69) <0·96>		− 191·29955 (18·2) <0·80>
UHF/6–311G(2d,p)		− 191·38286 (0·00) <0·95>		− 191·38195 (0·57) <0·95>		− 191·35358 (18·4) <0·80>
UMP2/6–31G★	− 191·86098 (0·00)	− 191·85885 (1·34)	− 191·85982 (0·73)	− 191·85797 (1·88)	− 181·84020 (12·3)	− 191·83730 (13·0)

[a] Total energies are in hartree; the relative energies are given in parentheses in kcal mol^{-1} and the $<S^2>$ values are given in angle brackets.

Table 3 Calculated structural parameters for the 1-hydroxylallyl radicals **2ss, 2sa, 2as** and **2aa** and transition structures **4a** and **4s**

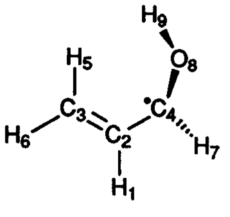
Parameter[a]	**2ss**	**2sa**	**2as**	**2aa**	**4a**	**4s**
H_1—C_2	1·076	1·077	1·080	1·077	1·081	1·082
C_2—C_3	1·392	1·390	1·393	1·289	1·324	1·324
C_2—C_4	1·384	1·384	1·381	1·384	1·480	1·484
C_4—O_8	1·351	1·358	1·353	1·358	1·366	1·365
H_5—C_3	1·076	1·073	1·072	1·073	1·076	1·076
H_6—C_3	1·073	1·074	1·073	1·073	1·076	1·076
H_7—C_4	1·071	1·074	1·072	1·075	1·084	1·075
H_9—O_8	0·947	0·945	0·948	0·945	0·947	0·948
H_1—C_2—C_3	117·87	118·94	117·92	119·19	119·27	119·30
H_1—C_2—C_4	115·13	115·80	117·61	116·53	117·23	117·37
C_2—C_4—O_8	125·80	120·43	124·67	119·67	114·58	118·27
H_5—C_3—C_2	123·06	121·28	121·41	121·56	121·59	121·60
H_6—C_3—C_2	120·71	120·77	121·04	121·09	121·56	121·865
H_7—C_4—C_2	122·29	122·40	123·15	122·92	118·61	118·27
C_4—O_8—H_9	111·13	110·56	110·70	110·48	109·86	109·55
H_1—C_2—C_4—H_7	0·00	0·00	180·00	180·00	− 59·68	− 58·79
H_1—C_2—C_4—O_8	180·00	180·00	0·00	0·00	82·47	81·49
C_2—C_4—O_8—H_9	0·02	179·92	− 0·06	180·00	− 176·67	33·51

[a] Bond lengths in Å, bond angles in degrees.

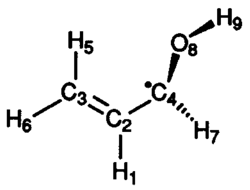
in Table 2. It must be noted that at the UHF level stereoisomer **2sa** is always lower in energy than **2aa**, and that the differences in relative energies at the different basis set levels are negligible.

Calculations were also carried out to locate the transition structures for the rotational isomerization of the *anti*- and *syn*-1-hydroxyallyl radicals. Two structures were located having the structures depicted in **4s** and **4a**, both of which possess one imaginary frequency. The total energies are given in Table 2 and the calculated structural parameters in Table 3. It should be noted that the UHF transition structures do not deviate significantly from 'C_s' symmetry as indicated by the similarity in the H_1—C_2—C_4—H_7 and H_1—C_2—C_4—O_8 dihedral angles.

A comparison of the energy barriers for rotational isomerization of the allyl and the 1-hydroxyallyl radicals **2sa→4a** and **2aa→4a** at the various levels of theory appears in Table 5. For the rotational isomerization of **2sa** via transition structure **4a** the presence on the 1-hydroxy group is calculated to result in a slight *increase* in the energy barrier, whereas in the rotational isomerization of **2aa** via **4a** the presence of the 1-hydroxy group is predicted to result in a slight *decrease* (0·2 kcal mol^{-1}) in the energy barrier. The reported experimental results indicate that the energy barriers for the rotational isomerization of both the *anti* and



4s



4a

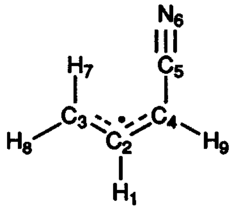
Table 4 π and σ Mulliken populations (MP) of the 1-hydroxyallyl radicals **2ss, 2sa, 2as** and **2aa**

MP	**2ss**	**2sa**	**2as**	**2aa**
$\pi(C_3—O_8)$	+0·0011	+0·0009	+0·0015	+0·0001
$\sigma(C_3—O_8)$	− 0·0026	+0·0001	− 0·0002	+0·0004
$\sigma(H_9—C_2)$	+0·0054	+0·0003	+0·0001	− 0·0002
$\sigma(H_1—H_9)$	− 0·0000	+0·0033	0·0000	− 0·0001
(Total)	+0·0031	+0·0046	+0·0013	+0·0003

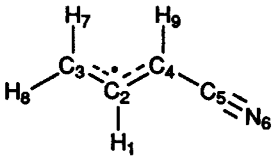
Table 5 Comparison of the calculated energy barriers[1] for the rotational isomerization of the allyl and 1-hydroxyallyl radicals

Method/basis set	Allyl	**2sa→4a**	E_a	**2aa→4a**	E_a
UHF/6–31G*	18·6	18·7	+0·1	18·3	− 0·3
QCISD(T)/6–31G*	15·0	15·3	+0·3	14·8	− 0·2
UHF/6–31+G*	18·4	18·9	+0·5	18·2	− 0·2
UHF/6–31++G*	18·3	18·2	− 0·1	17·5	− 0·8
UHF/6–311G(2d,p)	18·0	18·4	+0·4	17·8	− 0·2
UMP2/6–31G*	12·7	13·5	+0·8	12·9	+0·2

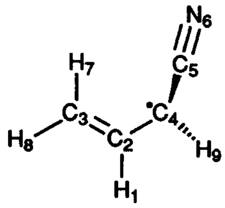
[a] Energies are given in kcal mol^{-1}.



5s



5a



6

syn conformations of the 1-methoxyallyl radicals are slightly lowered relative to that of the allyl radical.[10]

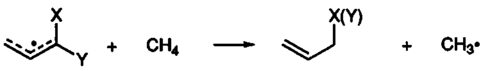
The effect of the 1-hydroxy group on the relative stability of the allyl radical can be assessed from the total changes in energy for the two isodesmic reactions shown in equations (6) and (7). The changes in total energy for these equations are given in Table 6. The large positive changes in total energies (endothermic), indicate that the 1-hydroxy group provides considerable ground-state stabilization to the 1-hydroxyallyl radical system. (For comparison purposes, the hydroxyl group is calculated to stabilize the methyl radical by only 5·3 kcal mol^{-1}.)[1]

The 1-cyanoallyl radical system

Calculations on the *syn*- and *anti*-stereoisomers of the 1-cyanoallyl radicals **5s** and **5a**, and on the transition structure **6** were carried out at the QCISD(T)/6–31G*// UHF/6–31G* level of theory. The total and relative energies are given in Table 7 and the calculated structural parameters in Table 8.

In contrast to the 1-hydroxyallyl radical, in which the *syn*-alloxy stereoisomers **2ss** and **2sa** were lower in energy than the *anti* stereoisomers **2as** and **2aa**, the *anti*-1-cyanallyl radical **5a** is lower in energy than the *syn*-stereoisomer. This appears to be due to long-range repulsive interactions between N_6 and C_3, as indicated by the MPs between N_6 and C_3, which are in closer proximity in **5s** than in **5a**.

The energy barriers for the rotational isomerization of **5a** and **5s** via **6** are 16·2 andf 15·7 kcal mol^{-1} at the UHF/ 6–31G* level and 12·5 and 12·2 kcal mol^{-1} at the QCISD(T)/6–31G* level of theory. The QCISD(T)/6–G* rotational energy barriers are 2·7 and 1·6 kcal mol^{-1} higher than the experimentally observed values and are 2.5–2·9 kcal mol^{-1} lower than the energy barriers calculated for the rotational isomerization of the allyl radical at the



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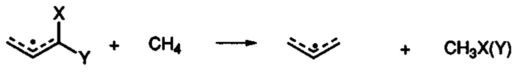


(7)

Table 6 Changes in total energy [QCISD(T), kcal mol^{-1}] for the isodesmic relationships in equations (4) and (5)

Structure	Equation (4)	Equation (5)
2sa (X = OH, Y = H)	+25·4	+11·3
2aa (X = H, Y = OH)	+24·9	+10·8
5s (X = CN, Y = H)	+25·1	+7·7
5a (X = H, Y = CN)	+25·3	+8·0

Table 7 Total and relative energies and UHF/$<S^2>$ values for the 1-cyanoallyl radical species

Species	*E*(SCF)	$<S^2>$	E_a	*E*[QCISD(T)]	E_a
5a	− 208·21120	1·10	0·00	− 208·89691	0·00
5s	− 208·21038	1·10	0·51	− 208·89648	0·37
6	− 208·18556	1·00	16·18	− 208·87704	12·46

Table 8 Calculated structural parameters of the 1-cyanoallyl radical species

Parameter[a]	5a	5s	6
H_1—C_2	1·076	1·076	1·079
C_2—C_3	1·380	1·381	1·325
C_2—C_4	1·405	1·407	1·486
C_4—C_5	1·413	1·417	1·397
C_5—N_6	1·150	1·149	1·158
C_3—H_7	1·075	1·074	1·076
C_3—H_8	1·073	1·073	1·075
C_4—H_9	1·075	1·073	1·076
H_1—C_2C_3	119·03	118·59	120·01
H_1—C_2C_4	117·79	116·00	116·22
C_2—C_4—C_5	112·43	123·24	122·11
C_4—C_5—N_6	179·63	179·73	179·60
C_2—C_3—H_7	121·28	121·70	122·02
C_2—C_3—H_8	120·77	120·70	121·06
C_2—C_4—H_9	122·40	120·41	120·60
H_1—C_2—C_4—C_5	0·00	180·00	87·14
C_2—C_4—C_5—H_6	0·00	180·00	87·38

[a] Bond lengths in Å, bond angles in degrees.

same level of theory. These calculated lowerings in the energy barriers are considerably smaller than those observed experimentally of 5·9 and 5·1 kcal mol^{-1}.[11,12]

The effect of the 1-cyano group on the relative energy of the allyl radical was estimated from the isodesmic relationships in equations (6) and (7). The changes in total energy are given in Table 6. The 1-cyano group is calculated to stabilize the ground state of the allyl radical by an amount of energy very similar to that provided by the 1-hydroxyl group.

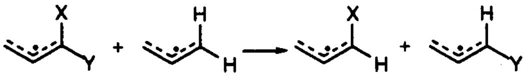
The 1-cyano-1-hydroxyallyl radical system

Calculations were carried out at the QCISD(T)/6–31G*// UHF/6–31G* level of theory on the *anti*- and *syn*-1-cyano-1-hydroxyallyl radicals having the conformations about the C_4—O_7 bond as shown in **7a** and **7s**, and on the rotational isomerization transition structure **8**. The total and relative energies are given in Table 9 and the calculated structural parameters in Table 10.

The calculated energy barriers for the rotational isomerization of **7s** and **7a** are 10·47 and 9·06 kcal mol^{-1}, respectively, compared with the experimentally observed values of 6·0 and 6·1 kcal mol^{-2}. Again, the calculated energy barriers are larger than the experimental values, but are considerably smaller than the calculated barriers for rotational isomerization of the 1-cyano- and 1-hydroxyallyl radicals.

The sum of the decreases in the energy barriers for the rotational isomerization of the 1-cyano and 1-hydroxyallyl radical systems relative to that of the allyl radical range from 2·3 to 2·8 kcal mol^{-1}. The decreases in the energy barriers for the rotational isomerization of the 1-cyano-1-hydroxyallyl radicals **7s** and **7a** are 4·5 and 5·9 kcal mol^{-1}. Hence there is an 'extra' lowering of the energy barrier for the rotational isomerization of **7s** and **7a** over the sum of the decreases in the energy barriers for the rotational isomerization of the 1-cyano- and 1-hydroxyallyl radicals in the range 2·2–3·1 kcal mol^{-1}.

However, this does not necessarily imply that there is captodative stabilization of the transition structure **8**. The effect of the two substituents on the relative stability of the ground states of **7s** and **7a** and the transition structure **8** can be assessed by considering the overall changes in energy for the isodesmic relationships shown in equations (8) and (9).



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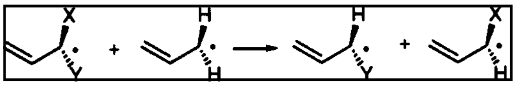
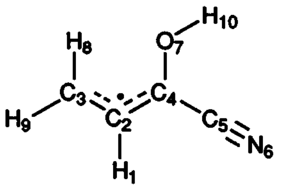
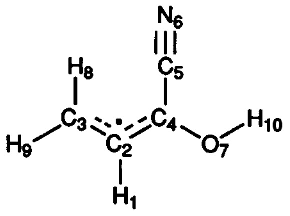


(9)

The overall changes in energy are given in Table 11. For both **7s** and **7a** in equation (8) the overall reactions are calculated to be slightly exothermic, indicating that captodative substitution in **7s** and **7a** does *not* result in enhanced stabilization of the allyl radical system relative to the effects of the individual functional groups on the relative stability of the allyl radical, but, in fact results in slight destabilization. The smaller E_a calculated for **7s** compares with that calculated for **7a** suggests that **7s** should possess a larger energy barrier for rotational isomerization than that for **7a**. The experimental values are, however, within experimental error of each other. For the isodesmic reaction shown in equation (9), this reaction is also exothermic, indicating that captodative substitution in the transition structure **8** does not result in any extra stabilization over and above that present in the transition structures for rotational isomerization of the 1-cyano- and 1-hydroxyallyl radicals.



7a



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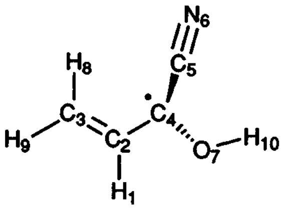

8

Table 9 Total and relative energies and $<S^2>$ values for the 1-cyano-1-hydroxyallyl radical species

Species	E(SCF)	$<S^2>$	E_a	E[QCISD(T)]	E_a
7s	− 283·05885	1·40	0·00	− 283·92950	0·00
7a	− 283·05600	1·12	1·79	− 283·92726	1·41
8	− 283·03489	0·96	15·03	− 283·91281	10·47

Table 10 Calculated structural parameters for the 1-cyano-1-hydroxyallyl radical species

Parameter^1	**7a**	**7s**	**8**
H_1—C_2	1·075	1·075	1·078
C_2—C_3	1·378	1·376	1·324
C_2—C_4	1·406	1·408	1·481
C_3—H_5	1·073	1·075	1·075
C_3—H_6	1·073	1·073	1·075
C_4—C_7	1·416	1·417	1·397
C_7—N_8	1·150	1·149	1·158
C_4—O_9	1·351	1·353	1·351
O_9—H_{10}	0·948	0·948	0·949
H_1—C_2—C_3	119·94	119·88	120·37
H_1—C_2—C_4	116·13	114·80	116·68
C_2—C_3—H_5	121·51	122·08	121·93
C_2—C_3—H_6	120·48	120·39	121·13
C_2—C_4—C_7	122·06	123·64	123·11
C_4—C_7—N_8	178·65	180·00	178·69
C_2—C_4—O_9	119·39	117·88	116·52
C_4—O_9—H_{10}	111·60	111·63	111·32
H_1—C_2—C_4—C_7	180·01	180·01	82·13
H_1—C_2—C_4—O_9	180·02	180·01	−91·45
C_2—C_4—O_9—H_{10}	180·02	180·01	177·60

[a] Bond lengths in Å, bond angles in degrees.

CONCLUSION

Why is there such a difference between the ‘gas-phase’ calculated energy barriers for rotational isomerization compared with the experimentally observed values? It was suggested previously that the effect of substituents should be greater in the transition structures for rotational isomerization than in the ground states of the substituted allyl radicals because in the transition structures the spin density on C_1 should be 1·0 (disregarding any delocalization with the attached substituents).[11,12] The results of the calculations on the isodesmic reactions shown in equations (8) and (9) suggest that such is not the case, in particular, the similarity between the ΔEs for **7a** in equation (8) and **8** in equation (9).

The experimental ESR studies were carried out in tetrahydrofuran solutions. The differences between the calculated and the experimentally observed energy barriers for rotational isomerization could well be due to differences in the solvent interactions with the ground-state versus the transition structures. There are significant differences in the change in the dipole moments of the ground-state and transition structures which are illustrated in Table 12.

Table 11 Changes in total energy [QCISD(T), kcal mol^{-1}] for the isodesmic relationships shown in equations (6) and (7)

Equation	Structure	E_a
(6)	**7s** (X+CN, Y=OH)	−1·08
(6)	**7a** (X=OH, Y=CN)	−3·23
(7)	**8** (X=CN, Y=OH)	−3·28

Table 12 Comparison of the calculated energy barriers (E_a) for rotational isomerization of the substituted allyl radicals with the change in dipole moments (μ) on going from the ground-state to the transition structures

Radical	E_a (kcal mol^{-1})	ΔE_a (kcal mol^{-1})	μ (D)
Allyl	15·0	0·0	+0·199
2aa	14·8	−0·2	−0·304
5a	12·5	−2·5	−0·348
7a	9·1	−5·9	+0·067
7b	10·5	−4·5	+1·0432

The results of this and previous theoretical studies carried out by the author on disubstituted methyl radicals and disubstituted ethenes do not lend support for the universal existence of the captodative concept. It must be recognized that the effect of substituents on the relative energies of the ground states of the reactants must also be seriously taken into consideration.

REFERENCES

1. D. J. Pasto, R. Krasnansky and C. Zercher, *J. Org. Chem.* **52**, 3062 (1987).
2. D. J. Pasto, *J. Am. Chem. Soc.* **111**, 7558 (1989).
3. F. G. Bordwell and T.-Y. Lynch, *J. Am. Chem. Soc.* **111**, 7558 (1989).
4. R. Sustmann and H.-G. Korth, *Adv. Phys. Org. Chem.* **26**, 131 (1990).
5. H. G. Viehe, Z. Janousek, R. Merenyi and L. Stella, *Acc. Chem. Res.* **18**, 148 (1985).
6. G. Leroy, M. Sana, C. Wilante and R. M. Memba, *J. Mol. Struct. (Theochem)* **198**, 159 (1989); G. Leroy, M. Sana, C. Wilante, D. Peeters and C. Dogimont, *J. Mol. Struct. (Theochem)* **153**, 249 (1987); G. Leroy, C. Wilante, D. Peeters and M. M. Ueyawa, *J. Mol. Struct. (Theochem)* **124**, 107 (1985); G. Leroy, D. Peeters and C. Wilante, *J. Mol. Struct. (Theochem)* **88**, 217 (1982); G. Leroy, *J. Mol. Struct. (Theochem)* **168**, 77 (1988); *Adv. Quantum Chem.* **17**, 1, (1985); *Bull. Soc. Chim. Belg.* **94**, 945 (1985); *Int. J. Quantum Chem.* **23**, 271 (1985).
7. D. Crans, T. Clark and P. v. R. Schleyer, *Tetrahedron Lett.* **21**, 3681 (1980).
8. L. Stella, Z. Janousek, R. Merenyi and H. G. Viehe, *Angew. Chem. Int. Ed. Engl.* **17**, 691 (1978); H. G. Viehe, R. Merenyi and L. Stella, *Angew. Chem. Int. Ed. Engl.* **18**, 917 (1979).
10. H.-G. Korth, H. Trill and R. Sustmann, *J. Am. Chem. Soc.* **103**, 4483 (1981).
11. R. Sustmann and H. Trill, *J. Am. Chem. Soc.* **96**, 4343 (1974).
12. H.-G. Korth, P. Lommes and R. Sustmann, *J. Am. Chem. Soc.* **106**, 663 (1984).
13. D. J. Pasto, *J. Org. Chem.* **57**, 139 (1992).
14. D. J. Pasto, F. Cottard and C. Picconatto, *J. Org. Chem.* **59**, 7172 (1994);
15. Pasto, D. J. *J. Org. Chem.* **61**, 252 (1996).
16. M. J. Frisch, G. W. Trucks, H. B. Schelegel, R., M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Kieth, G. A. Petersson, J. A. Montergomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrewski, J. V. Ortiz, J. B. Foresman, C. Y.

Peng, P. Y. Ayala, W. Chen, M. Wong, W, J. Andres, L, Replople, E. S. Gomperts, R. L. Martin, O. J. Fox, J. S. Binckley, D. Jo Defrees, J. Baker, Head-Gordon M. Stewart, C. Gonazalez and J. A. J. Pople, *Gaussian 94, Revision B.3.* Gaussian, Pittsburgh, PA (1995).

17. D. A. Hrovat and W. T. Borden, *J. Phys. Chem.* **98**, 10460 (1994); A. Gobbi and G. Frenking, *J. Am. Chem. Soc.* **116**, 9275 (1994); S. S. Shaik, P. Hiberty, J.-M. Lefour and G. Ohanessian, *J. Am. Chem. Soc.* **109**, 363 (1987); O. Kikuchi, *Chem. Phys. Lett.* **72**, 487 (1982); J. Paldus and A. Veillard, *Chem. Phys. Lett.* **50**, 6 (1977); *Mol. Phys.* **35**, 445 (1978); J. McKelvey and G. Berthier, *Chem. Phys. Lett.* **41**, 476 (1976); H. M. McConnell, D. B. Chestnut, *J. Chem. Phys.* **28**, 107; G. Levin and W. A. Goddard III, *J. Am. Chem. Soc.* **97**, 1649.