Tetrahedron. Vol 33, pp 2497 to 2501. Pergamon Press 1977. Printed in Great Britain

GEOMETRICAL PREFERENCES OF THE CROTYL ANION, RADICAL AND CATION

PAUL V.R. SCHLEYER*
Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestr. 42, D-8520 Erlangen, West Germany

JAMES D. DILL
Department of Chemistry, Princeton University, Princeton, NY 08540, U.S.A.

JOHN A. POPLE
Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA 15213, U.S.A.

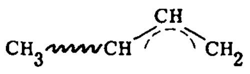
and

WARREN J. HEHRE
Department of Chemistry, University of California, Irvine, CA 92717, U.S.A.

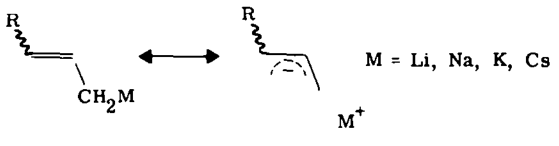
(Received in the USA 1 March 1977; Received in the UK for publication 28 March 1977)

Abstract—*ab initio* MO calculations have been performed on the *cis* and *trans* isomers of the crotyl cation, free radical and anion in each of two orientations of the Me rotor about the allylic framework. In agreement with available experimental data, both the crotyl cation and free radical prefer *trans* skeletal geometries. On the other hand, the *cis* isomer of the crotyl anion is found to be more stable than the *trans*, the same preference as has been noted for alkali metal allyl organometallics in solution, but opposite to that recently reported for the free (gas phase) anion. The Me groups are predicted to eclipse the partial double bond for the *trans* isomers of all three systems and for the *cis* cation. These results are rationalized with the aid of perturbation MO theory.

The crotyl system (1-methylallyl, **1**) shows a marked geometrical sensitivity to π electron occupancy.[1–6] Experimental evidence indicates that the crotyl cation (2π electrons on allyl) favors a *trans* skeletal geometry over a *cis* arrangement by at least 2 kcal/mol.[4] The crotyl free radical (3π electrons on allyl) also prefers to be *trans*, but only by about 0.2 kcal/mol.[5] In contrast, a wide variety of alkali metal allyl organometallics (**2**)[1–3] exhibit distinct and often sizable preferences for *cis* skeletal arrangements. For example, the potassium salt of the crotyl anion (**2**, R=Me, M=K) shows a free energy preference of 2.2 kcal/mol for a *cis* geometry over a *trans*.[1e] Similar *cis* energy preferences have been noted for other alkali metal salts of the crotyl system, and for the salts of more highly substituted alkenyl organometallics. Recent measurements by ion cyclotron resonance (icr) spectroscopy[7] of the relative acidities of *cis* and *trans* 2-butene indicate, however, that, in the gas phase, the free energy of the *trans* crotyl anion is some 0.2 kcal/mol lower that that for the *cis*. The authors have noted, however, that the icr experiment provides no information other than mass regarding the identities of the ions under investigation. Thus, it is conceivable that the *cis* and *trans* crotyl anions, formed by deprotonation of their respective alkenes, have undergone isomerization, or have reprotonated to form 1-butene instead of *cis* and *trans* 2-butene, respectively. In either case the resulting thermodynamic estimate of the relative stabilities of the isomeric crotyl anions would be in error.



1



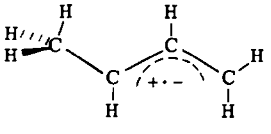
2

In this paper we describe the results of our theoretical studies on the relative stabilities of the *cis* and *trans* isomers of the crotyl cation, free radical and anion. The latter system is especially interesting in view of the discrepancy between the available solution and gas phase data. We shall also be concerned with the related question of the conformation of the Me rotor in each of these systems. Previous theoretical work[8] has suggested the rationale behind the known tendency for Me group to eclipse rather than to stagger double bonds, and at the same time has demonstrated the connection between the magnitude of the conformational preferences and the polarity of the unsaturated linkage. The same arguments—based on simple perturbation MO theory—applied for molecules such as propene should also be of use here.

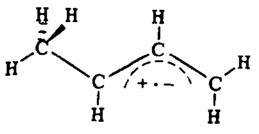
METHODS, RESULTS AND DISCUSSION

Ab initio MO calculations have been performed on each of four structures for the crotyl cation, free radical and anion.

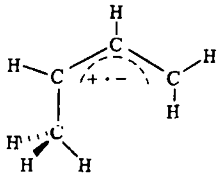
Four levels of theory have been utilized in our study: **A**, STO-3G minimal basis set[9] with standard model geometries[10] which are assumed to be identical for the cation, free radical and anion; **B**, STO-3G basis set and independent optimization of skeletal (CCC) bond angles in each system; **C**, split-valence-shell 4-31G basis set,[11]



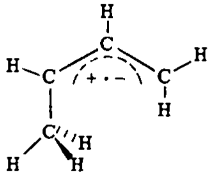
trans eclipsed



trans staggered



cis eclipsed



cis staggered

and geometries from level B (only the lower energy rotamer for each of the cation, free radical and anion has been considered) and; **D**, 4-31G, with partial optimization of skeletal bond angles and other geometrical parameters with this basis set[12] (only for the lower energy rotamer for each of the *cis* and *trans* crotyl anion). All calculations have been performed using the Gaussian 70 series of computer programs.[13] Our energy and geometry data are presented in Table 1.

The constraint placed on the calculations at level A, that the same fixed model geometries are employed for the cation, free radical and anion, should effect a separation of steric factors from other electronic dictates. It is easily seen (Table 1) that π electron occupancy does, in fact, markedly alter the *cis-trans* energy difference. Although, at this level of calculation, all three crotyl systems preferentially adopt *trans* skeletal geometries, *cis-trans* energy separations range from 5.2 kcal/mol for the cation, to 2.2 kcal/mol for the free radical and 0.7 kcal/mol for the anion. Unfavorable steric interactions, resulting from our use of standard model rather than optimized geometries, are expected to be more significant for the *cis* isomers than for the corresponding *trans* systems. It is not surprising, therefore, that the theoretical *cis-trans* energy differences obtained at level A are reduced somewhat (to 3.5, 1.3 and 0.3 kcal/mol for the crotyl cation, free radical and anion, respectively) upon optimization of the two skeletal bond angles in each system. Still, the prediction of the minimal basis set STO-3G method is that all three systems favor a *trans* skeletal arrangement, this preference being largest for the cation and smallest for the anion. Whereas the split-valence-shell 4-31G calculations serve only to support the findings of the minimal basis set theory regarding the preferred skeletal arrangements for the crotyl cation and free radical (the *trans* isomers are preferred by 3.4 and 1.0 kcal/mol, respectively), they contest its conclusions for the corresponding anion. Utilizing skeletal bond angles optimized at STO-3G, the 4-31G *level calculations indicate the* cis *isomer of the crotyl anion to be favored over the* trans *by* 1.5 *kcal/mol.* Bond angle optimization using the 4-31G method itself lowers this difference only slighly (to 1.4 kcal/mol). The 4-31G results (levels C and D) appear to agree reasonably well with the available solution phase experimental data on alkali metal organometallics although they take issue with the recent icr determination of the relative stabilities of the *cis* and *trans* crotyl anions. The reason for this latter discrepancy remains unclear.

A number of authors have already put forth rationalizations for the isomeric preferences noted for these and related systems.[6] In the most simple terms, these are based on the notion that the *cis* isomers of molecules such as the crotyl systems are comprised of cyclical arrangements of π electrons and, hence, have the potential to be aromatic or antiaromatic in character. Thus, in its *cis* skeletal form, the crotyl cation has 4π (4N) electrons available for cyclic conjugation (2 from the allyl moiety and 2 from Me), making it an antiaromatic. Therefore, quite aside from steric considerations, it has ample reason to prefer a *trans* geometry. On the other hand, the crotyl anion has 6π (4N + 2) electrons. It might be expected to show some aromaticity, therefore, favoring a *cis* carbon skeleton, the arrangement of atoms which maximizes the extent of cyclic conjugation.

Closely associated with the noted *cis* or *trans* energy preferences in the crotyl systems is the question of the equilibrium conformation of the Me rotor be it staggered (S) or eclipsed(E). In the *trans* isomers interaction between the Me rotor and the allyl frameworks appears to be slight, with torsional barriers (levels A and B) ranging from 0.5 to 1.1 kcal/mol, and largely independent of total charge. In all three systems eclipsed forms are preferred over staggered rotamers, consistent with the observed equilibrium conformations of molecules in which Me groups are attached to unsaturated linkages. For comparison, torsional barriers in systems such as propene and *trans* 2-butene (1.55 and 1.54 kcal/mol, respectively, as calculated at level B)[14] are of the same order of magnitude but somewhat larger. According to the fixed geometry (level A) calculations, all three systems prefer staggered Me conformations, with barriers ranging from 2.3 kcal/mol for the cation to 5.5 kcal/mol for the anion. It appears, therefore, that increase in the π electron population of the allylic framework to which the Me rotor is attached furthers the trend toward a staggered conformation. Optimization of skeletal bond angles (level B) not only leads to a lowering of the torsional barriers in the three systems, but also succeeds in upsetting the prediction of the level A calculations regarding the conformation of the Me rotor in the *cis* crotyl cation. Thus, whereas both the *cis* crotyl free radical and the corresponding anion adopt conformations in which the Me group staggers the partial double bond of the allylic moiety (with torsional barriers to the respective eclipsed arrangements of 0.14 and 0.13 kcal/mol), the *cis* isomer of the crotyl cation remains eclipsed with a larger (0.57 kcal/mol) rotation barrier to a staggered form.

The theoretically predicted equilibrium Me group conformations of the crotyl systems are easily rationalized in terms of previously advanced arguments.[8] Thus, the *trans* crotyl systems, in which the possibility for cyclic conjugation is non-existent, adopt eclipsed rotor conformations for essentially the same reasons as do molecules such as propene. In the language of perturbation MO theory, energetic stabilization or destabilization results from interaction of the π orbitals of the allylic framework with the valence manifold on Me (Fig. 1). Of the possible interactions between the two sets of valence molecular orbitals only three are pertinent to the question of Me group conformation. Interaction 1 (between π_1 on allyl and π_{CH_3}) is 4-electron destabilizing. The conformer (eclipsed or staggered) with the greater effective overlap will be the more disfavored. This will be the staggered form because of overlap, not available to the eclipsed, between the Me group CH bonds and the central p lobe of the allyl skeleton.

Table 1. *Ab initio* calculations on crotyl systems ($^{4}CH_3\ {}^{1}CH \overset{2}{=\!=} CH \overset{3}{=\!=} CH_2$)

Species	Conformation[a]	A[b]	B[b]			C[b]	D[b]		
		E (ΔE)[c]	E (ΔE)[c]	α[d]	β[d]	E (ΔE)[c]	E (ΔE)[c]	α[e]	β[e]
Cation									
Trans	E	-153.413460 (0.0)	-153.414365 (0.0)	124.4	118.9	-155.027094 (0.0)			
Trans	S	-153.412406 (0.66)	-153.413043 (0.83)	123.7	118.9				
Cis	E	-153.401615 (7.43)	-153.409638 (2.97)	129.1	122.4	-155.021738 (3.36)			
Cis	S	-153.405219 (5.17)	-153.408721 (3.54)	127.3	121.5				
Radical									
Trans	E	-153.637603 (0.0)	-153.639344 (0.0)	124.0	124.1	-155.286201 (0.0)			
Trans	S	-153.636801 (0.50)	-153.638179 (0.73)	123.0	124.2				
Cis	E	-153.627865 (6.11)	-153.637075 (1.42)	126.4	127.2				
Cis	S	-153.634092 (2.20)	-153.637303 (1.28)	124.2	125.7	-155.284566 (1.02)			
Anion									
Trans	E	-153.412181 (0.0)	-153.419690 (0.0)	123.6	131.3	-155.201724 (1.48)	-155.201922 (1.40)	124.4	133.0
Trans	S	-153.410772 (0.88)	-153.417945 (1.09)	122.6	131.4				
Cis	E	-153.402312 (6.19)	-153.419071 (0.39)	125.1	133.4				
Cis	S	-153.411032 (0.72)	-153.419276 (0.26)	123.0	131.7	-155.203986 (0.0)	-155.204149 (0.0)	122.0	131.7

[a] Methyl group (^{4}C) eclipsed (E) or staggered (S) relative to the $^1C^2C$ bond. *Trans* and *cis* refer to the CCCC configuration. [b] Level A: STO-3G basis standard geometries.[10] Level B: STO-3G basis, optimized CCC angles α and β. Level C: 4-31G basis using Level B geometries. Level D: 4-31G basis, partial optimization of skeletal bond angles and other geometrical parameters. [c] E in hartrees, ΔE in kcal/mol. [d] At levels B and C, optimized $^4C^1C^2C$ (α) and $^1C^2C^3C$ (β) angles. Other angles: $H^4C^1C = 109.4712°$, $H^2C^3C = 180° - \alpha/2$, $H^2C^3C = 180° - \beta/2$, $H^3C^2C = 120°$. [e] See footnote 12 for details of other geometrical parameters.

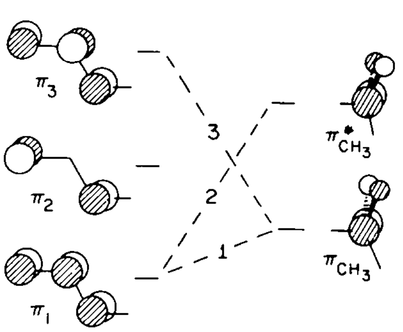
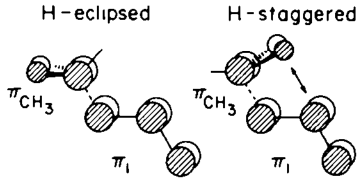
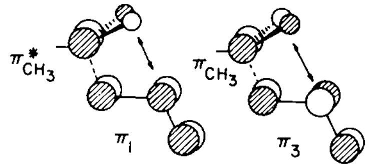


Fig. 1. Interaction of allylic π orbitals with the valence molecular orbitals on a Me group. See text for explanation.

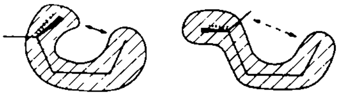


Interactions 2 and 3 (between π_1 and $\pi^*_{CH_3}$ and π_3 and π_{CH_3}) are 2-electron stabilizing. They will be of most benefit in that situation where total overlap is at a maximum. In both cases this is for the eclipsed conformer, for the small overlap component involving the Me CH linkages and the allylic skeleton is of opposite sign to the principal overlap (between centers already bonded via the σ framework) and hence subtracts from the total.



Interactions involving the second (non-bonded) π level of allyl are of no consequence to Me group conformation; there is no density on the central atom visible to the Me rotor. Because interactions involving the allyl π_2 level play no part in dictating rotor conformation, the perturbation arguments also suggest that the Me group torsion barriers in each of the three crotyl systems should be of comparable magnitude. The data in Table 1 support such a contention. Finally, although interaction between π_3 and $\pi^*_{Me_3}$ would result in a preference for a staggered rotor conformation, neither level is occupied and, therefore, no net stabilization or destabilization results.

The Me rotor preferences noted for the crotyl systems in their *cis* geometries may also be rationalized with the aid of interaction diagrams similar to that presented in Fig. 1. The key feature is the overlap between the Me group and the far terminus of the allylic skeleton to which it is attached. This will be at a maximum for a staggered rotor conformation and at a minimum for an eclipsed arrangement.



For the cation (4π electrons) the resulting cyclic conjugation leads to energetic destabilization. Therefore, a eclipsed conformation of the Me rotor should be preferred, as indeed it is according the *ab initio* calculations. For the crotyl anion with its 6π electrons the situation is just the opposite. Here the potential for aromatic stabilization causes the Me rotor to stagger the allylic framework thus leading to maximum overlap with the far terminus. The quantitative calculations concur. The crotyl free radical with its 5π electrons shows only a slight preference for the Me group to adopt a staggered conformation.[15]

CONCLUSIONS

1. The preference for a *cis* or *trans* carbon skeleton depends on the formal charge of the allylic framework. The crotyl cation and free radical prefer *trans* geometries, but the crotyl anion favors a *cis* skeleton. These preferences may be rationalized by recognizing the possibility of cyclic conjugation (aromaticity or antiaromaticity) in the *cis* isomers.

2. The Me group in the *trans* isomer of each system adopts a conformation in which one of its hydrogens eclipses the partial double bond, the same preference as in propene. The rotor in the *cis* crotyl cation also adopts an eclipsed conformation minimizing the extent of unfavorable (4π electron) cyclic conjugation. The situation is reversed for the *cis* crotyl anion, where conjugation, facilitated by a staggered Me, leads to aromatic stabilization.

Acknowledgements—Some of the calculations were carried out at the University of Munich, with the generous assistance of the Humboldt Foundation and the Leibniz Rechenzentrum. The research was supported by the National Science Foundation (Grants GP29078X, Princeton and CHE75-09808, Carnegie-Mellon) and by the Fonds der Chemischen Industrie (Erlangen). Discussions with Prof. K. Houk and Prof. M. Schlosser are gratefully acknowledged.

REFERENCES

[1] Anion, equilibrium preferences: [a] H. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas* **87**, 1025 (1968); [b] W. J. Glaze, J. E. Hanicak, J. Chaudhuri, M. L. Moore and D. P. Duncan, *J. Organometal. Chem.* **51**, 13 (1973), and earlier papers in this series; [c] D. A. Hutchinson, K. R. Beck, R. A. Benkeser and J. B. Grutzner, *J. Am. Chem. Soc.* **95**, 7075 (1973); [d] J. P. C. M. van Dongen and H. W. D. van Drunen, *Recl. Trav. Chim. Pays-Bas* **93**, 29 (1974); [e] M. Schlosser, J. Hartmann and V. David, *Helv. Chim. Acta* **57**, 1567 (1974); [f] R. B. Bates and W. A. Beavers, *J. Am. Chem. Soc.* **96**, 5001 (1974); [g] W. H. Glaze and D. P. Duncan, *J. Organomet. Chem.* **99**, 11 (1975); [h] D. H. O'Brien, C. R. Russell and A. J. Hart, *Tetrahedron Letters* 37 (1976); [i] M. Schlosser and J. Hartmann, *J. Am. Chem. Soc.* **98**, 4674 (1976). Also see W. T. Ford and M. Newcomb, *J. Am. Chem. Soc.* **96**, 309 (1974).

[2] Anion, kinetic preferences: [a] W. O. Hoag and H. Pines, *J. Am. Chem. Soc.* **82**, 387 (1960); [b] T. J. Prosser, *Ibid.* **83**, 1701 (1961); [c] C. C. Prince and W. H. Snyder, *Ibid.* **83**, 1773 (1961); [d] A. Schreisheim, J. E. Hofmann and C. A. Rowe, Jr., *Ibid.* **83**, 3731 (1961); [e] C. C. Prince and W. H. Snyder, *Tetrahedron Letters* **69**, (1962); [f] M. D. Carr, J. R. P. Clarke and M. F. Whiting, *Proc. Chem. Soc.* P333 (1963); [g] S. Bank, A. Schriesheim and C. A. Rowe, Jr., *J. Am. Chem. Soc.* **87**, 3244 (1965).

[3] Anion, reviews: [a] H. F. Ebel, *Fort. Chem. Fortsch.* **12**, 387 (1969); [b] L. A. Fedorov, *Russ. Chem. Rev.* **39**, 655 (1970); [c] K. Vrieze, *Dynamic Nuclear Magnetic Resonance Spectroscopy* (Edited by L. M. Jackman and F. A. Cotton) chap. 11. Academic Press, New York (1975): [d] M. Schlosser, *Polare Organometalle*, Springer-Verlag, Berlin (1973).

[4] Cation: P. v. R. Schleyer, T. Su, M. Saunders and J. C. Rosenfeld, *J. Am. Chem. Soc.* **91**, 5174 (1969).

[5] Free radical: D. C. Montague, *Int. J. Chem. Kinetics* **5**, 513 (1973).

[6] Theoretical: [a]R. Hoffmann and R. A. Olofson, *J. Am. Chem. Soc.* **88**, 943 (1966); [b]I. Elphimoff-Felkin and J. Huet, *C. R. Acad. Sci. Ser. C* **268**, 2210 (1969); [c]J. R. Grunwell and J. F. Sebastian, *Tetrahedron* **27**, 4387 (1971); [d]N. D. Epiotis, D. Bjorquist, L. Bjorquist and L. Sarkanen, *J. Am. Chem. Soc.* **95**, 7558 (1973); [e]R. C. Bingham, *Ibid.* **98**, 535 (1976); [f]F. Bernardi, N. D. Epiotis, R. L. Yates and H. B. Schlegel, *Ibid.* **98**, 2385 (1976); [g]A. Sabljić, N. Trinajstić, J. V. Knop, J. Koller and A. Ažman, *J. Mol. Struct.* **33**, 145 (1976).

[7] J. Bartmess, W. J. Hehre, R. T. McIver, Jr. and L. E. Overman, *Ibid.* **99** (1977).

[8] [a]W. J. Hehre and L. Salem, *Chem. Commun.* 754 (1973), and Refs therein; [b]D. Cremer, J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.* **96**, 6900 (1974); [c]W. J. Hehre and J. A. Pople, *Ibid.* **97**, 6941 (1975); [d]W. J. Hehre, J. A. Pople and A. J. P. Devaquet, *Ibid.* **98**, 664 (1976); [e]W. J. Hehre, *Accounts Chem. Res.* **8**, 369 (1975).

[9] W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969).

[10] Geometrical assumptions: $C\text{–}CH_3 = 1.52$ Å, CC (allyl) = 1.40 Å, CH (allyl) = 1.08 Å, CH (Me) = 1.09 Å. All angles 120° at trigonal carbons, tetrahedral at Me carbons.

[11] R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.* **54**, 724 (1971).

[12] Geometrical assumptions: $C\text{–}CH_3 = 1.52$ Å, CH (allyl) = 1.10 Å, CH (Me) = 1.09 Å. Angles tetrahedral at Me carbon, C_2H bond bisects angle $C_1C_2C_3$. Angles $HC_3C_2 = 122°$. Calculated geometrical parameters: *cis*, $C_1\text{–}C_2 = C_2\text{–}C_3 = 1.38$ Å, $<HC_1C_2 = 119.0°$; *trans*, $C_1\text{–}C_2 = C_2\text{–}C_3 = 1.38$ Å, $<HC_1C_2 = 117.8°$.

[13] W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton and J. A. Pople, Gaussian 70, QCPE No. 236, *Quantum Chemistry Program Exchange*, Bloomington, Indiana.

[14] L. Radom and J. A. Pople, *J. Am. Chem. Soc.* **92**, 4786 (1970).

[15] Similar theoretical strudies on a number of 1,3-dimethylallyl isomers (J. D. Dill, Ph. D. Thesis, Princeton University, 1976) confirms and extends these conclusions. The preferred methyl group conformations in the sickle (*cis, trans*) isomers are quite like those found in the corresponding *cis* or *trans* crotyl anions, radicals, and cations. In contrast, this *cis, cis* (U-shaped) 1,3-dimethylallyl anion exhibits an electronic bias *against* the conformation in which both methyl groups are staggered. This quasi-cyclic 8 π electron arrangement would be destabilizing.