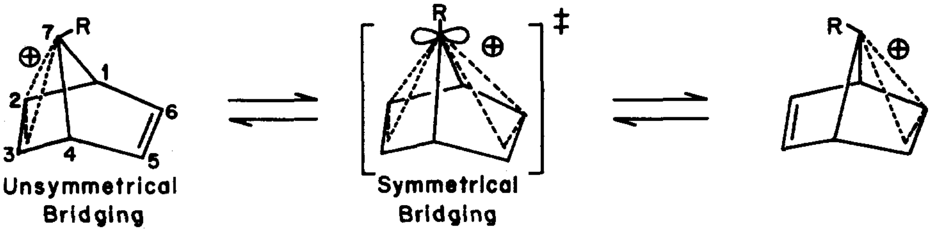
Tetrahedron Letters No.2, pp. 141-144, 1971. Pergamon Press. Printed in Great Britain.

THE 7-METHOXYNORBORNADIENYL CATION: EVIDENCE FOR A SYMMETRICALLY BRIDGED STRUCTURE

R. K. Lustgarten,[1a] M. Brookhart[1b] and S. Winstein[1c]
Department of Chemistry
University of California at Los Angeles
Los Angeles, California 90024

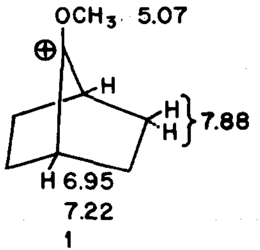
(Received in USA 2 November 1970; received in UK for publication 7 December 1970)

Many kinetic and stereochemical data, as well as direct spectroscopic observations, have accumulated to support the nonclassical, bridged nature of secondary[2] and some tertiary[3] 7-substituted-7-norbornenyl and 7-norbornadienyl carbonium ions. However, when a strongly charge stabilizing substituent is placed at C_7, stabilization due to the bridged interaction will be decreased and may actually be cancelled. This has been demonstrated for the 7-norbornenyl series by solvolytic studies[3a] and by direct nmr analysis of fully formed ions.[3b] In the 7-norbornadienyl series, the substituent effect has been illustrated by considering the barrier to "bridge-flipping" (eq. 1), the free energy difference between the unsymmetrical (ground state) and symmetrical (transition state) forms of the ion.[4a] For the parent cation, this difference must be 19.6 kcal/mole or more. For the 7-methyl ion, it is 12.4 kcal/mole, and for the 7-phenyl ion it is less than *ca*. 5.2 kcal/mole.[4b] This correlation between decreasing barriers to "bridge-flipping" and increasing stabilizing ability occurs because the substituents stabilize selectively the transition state (*i.e.*, the symmetrical form of the ion) in which delocalization of charge to the unsaturated linkages of the ring system is minimized and delocalization into the substituent is maximized. It is conceivable that, in the extreme where the substituent is very highly stabilizing, the symmetrically bridged ion will be more stable than the unsymmetrically bridged form.[3,5] This communication presents evidence that methoxyl is such a substituent.

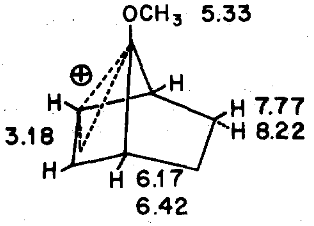


(1)

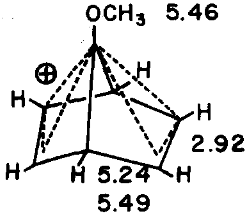
Each of the cations 1-3 was generated in FSO_3H solution by extraction of the corresponding ketal precursor from pentane or CD_2Cl_2 at -78°. Spectra were recorded at *ca*. -60°, and the chemical shifts were assigned (relative to internal CH_2Cl_2 at τ 4.70) as described on the appropriate structures. The nonequivalence of the bridgehead protons arises from the fact that, in order for p-p π overlap to occur between C_7 and oxygen, the methyl function must lie in the C_1-C_7-C_4 plane, and is thus oriented *syn* to one bridgehead proton and *anti* to the other. Upon warming the solutions, a degenerate *syn*-*anti* isomerization (indicated for 3 in eq. 2) was observed for all three ions. This phenomenon was manifested as a reversible coalescence of the signals for $H_{\underline{syn}}$ and $H_{\underline{anti}}$ with no change in the remainder of the spectrum. The pertinent experimental observations are given in the Table, along with the activation free energies for the process.



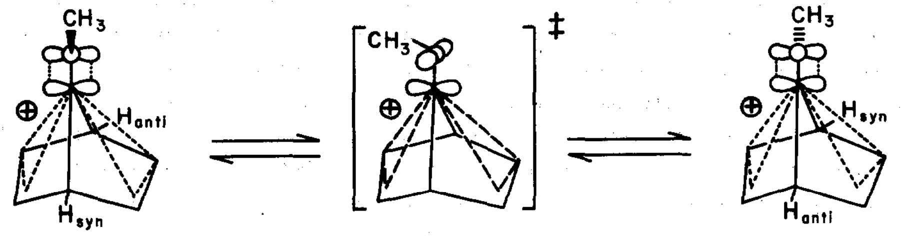
1



2



3



(2)

<u>Table</u>

Cation	Bridgehead Resonances (τ)	T_c^{a}	$k_{T_c}^{b}$ (sec^{-1})	$\Delta F^{\ddagger}$
1	6.95 7.22	+82 ± 7°^{c}	36	18.4
2	6.17 6.42	+12 ± 2°	29	14.7
3	5.24	-44 ± 2°	31	11.7

[a] Coalescence temperature for the two bridgehead resonances. [b] Rate constant for syn-anti isomerization at T_c. [c] This measurement is somewhat less precise than the others because signals resulting from decomposition of 1 appear in the same region as the bridgehead resonances.

The mechanism of this isomerization may involve rotation about the C_7-OMe bond, or it could be due to inversion at oxygen.[6] Whatever the precise mechanism, the point of critical interest is that the activation free energies for isomerization of 2 and 3 are significantly lower than for 1. We interpret this as being due to delocalization of charge into the unsaturated linkages during isomerization with consequent decreased demand on oxygen for stabilization of charge by p-p π overlap with C_7. The case for charge delocalization in the transition state is supported by comparison with other systems for which methoxyl "rotational" barriers[6] have been measured. For example, the 3-methoxycyclohexadienyl and 1,6-dimethyl-3-methoxycyclohexadienyl cations (HF-BF_3 medium) undergo the "syn-anti" equilibration with $\Delta F^{\ddagger}$ values of 13.0 and 11.4 kcal/mole, respectively,[7a] while the dimethoxy methyl and dimethoxy hydroxy carbonium ions (FSO_3H-SO_2-SbF_5) have $\Delta F^{\ddagger}$ values of 14.3 and 11.7 kcal/mole, respectively.[7b,c] On the other hand, the methoxyl signals in syn or anti-2-methoxy-2-norbornyl cation[8a] are unbroadened at

+80°,[8b] indicating that $\Delta F^\ddagger$ for "*syn*-*anti*" equilibration is $\geq$ *ca.* 19.5 kcal/mole. C-OH rotational barriers in hydroxy-carbonium ions also show a decrease in magnitude as the trigonal carbon is substituted with stronger stabilizing substituents.[7b]

As is the case for the 7-phenyl-7-norbornadienyl cation, the vinyl hydrogens of 3 show a single nmr resonance at low temperature, and hence the spectrum could be interpreted in terms of either a symmetrical ground state or a rapidly flipping pair of unsymmetrically bridged enantiomers ($\Delta F^\ddagger \leq$ *ca.* 7.6 kcal/mole). However, several features of the spectra support the view that the ground state of 3, unlike that of the 7-phenyl homolog,[3b,4a] is symmetrically bridged with full sp^2 hybridization at C_7. The OMe shifts of 1, 2 and 3 are typical for methoxyls attached to sp^2 cationic centers,[7a,b8] and they show a progressive upfield shift in keeping with the notion that charge is removed from C_7 through the series.[9] The splitting pattern of the vinyl hydrogens in 3 (a distinct triplet with 4.5 Hz spacing between outer lines) is diagnostic for the absence of unsymmetrical bridging, since those 7-substituted-7-norbornenyl and -dienyl ions which are known to be bridged display characteristic vinyl H absorptions as quartets or broadened triplets with a wider spacing between the outer lines (7.5 - 8.5 Hz) than do tetravalent analogs and those ions thought not to be bridged (triplets, spacing between outer lines 4-5 Hz).[3b,12]

A further argument favoring symmetrically bridged ground and transition states for 3 and reaction (2), respectively, derives from the data in the Table. If the ground state of 3 were unsymmetrically bridged, such bridging would only be strengthened in the transition state for (2), since charge becomes concentrated at C_7 during the isomerization and demand for delocalization is increased. The second double bond of 3 would then have little effect on the isomerization and similar activation barriers should result for 2 and 3. However, the barriers are significantly different. Furthermore, symmetrical bridging in 3 must be maintained in the transition state for (2); if it were replaced by unsymmetrical bridging, the net stabilization of 3 relative to 2 would be lost in their respective transition states, and $\Delta F^\ddagger$ would then be greater for 3 than for 2. The opposite result is obtained. We assume here that the increment represented by $\Delta\Delta F^\ddagger$ is essentially an isolated electronic factor. On this basis, the observed increase in rotational barrier in comparing 1 with 2 should be (and is) approximately equal to that between 2 and 3.

Finally, we note that the $\Delta F^\ddagger$ values for the conversion of 7-norbornadienyl cations to the corresponding tropylium ions are 23.5, 17.1, 15.9, and 24.2 kcal/mole for the parent,[13] 7-vinyl,[14] 7-phenyl,[4a] and 7-methoxy (3)[4a] ions, respectively. It is puzzling that vinyl and phenyl should cause a substantial lowering of the energy barrier for this process while methoxyl, an even better charge stabilizing substituent, should cause it to be raised again. It is tempting to suggest that an unsymmetrically bridged structure is a requisite geometry for this reaction. Tropylium ion formation from 3 may then appear inordinately slow because $\Delta F^\ddagger$ may contain a contribution from the strain and rehybridization energy necessary for constriction of the bridgehead angles whilst the other three cations contain the appropriate geometry in their ground states.

REFERENCES

1. a) NIH Postdoctoral Fellow, 1966-1968; address inquiries to this author at: Dept. of Chemistry, Carnegie-Mellon University, Pittsburgh, Pa. 15213; b) NSF Postdoctoral Fellow, 1968; present address: Dept. of Chemistry, University of North Carolina, Chapel Hill, N.C. 27514; c) Deceased, November 23, 1969.

2. S. Winstein, *Quart. Rev.* (*London*), **23**, 141 (1969), and references therein; b) P. G. Gassman and D. S. Patton, *J. Amer. Chem. Soc.*, **91**, 2160 (1969); c) R. K. Lustgarten, M. Brookhart, S. Winstein, P. G. Gassman, D. S. Patton, H. G. Richey, Jr., and J. D. Nichols, *Tetrahedron Letters*, 1699 (1970).

3. a) P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **91**, 1545; **92**, 2549 (1969); b) H. G. Richey, Jr., J. D. Nichols, P. G. Gassman, A. F. Fentiman, Jr., S. Winstein, M. Brookhart, and R. K. Lustgarten, *J. Amer. Chem. Soc.*, **92**, 3783 (1970).

4. a) M. Brookhart, R. K. Lustgarten, and S. Winstein, ibid., 89, 6352 (1967); 6354 (1967); b) This ion has now been observed at -140° with no broadening of the vinyl H signal. Hence, the lower value than previously estimated,[4a] M. Brookhart, unpublished results.

5. The term "unsymmetrical bridging" is here meant to imply a deliberate constriction of the angle between the C_1-C_7-C_4 and C_1-C_2-C_3-C_4 planes with incorporation of substantial s character in the p-orbital at C_7, as previously discussed.[2a] This geometry is to be distinguished from the "symmetrical" one which maintains sp^2 hybridization but which may nevertheless afford delocalization of charge to the vinyl function(s), e.g., **2** and **3**.

6. Recent CNDO calculations for protonated formaldehyde and acetaldehyde predict that the rotation mechanism is favored: K. F. Purcell and J. M. Collins, *ibid.*, **92**, 465 (1970).

7. a) D. M. Brouwer, E. L. Mackor, and C. Maclean, *Rec. Trav. Chim.*, **85**, 114 (1966); b) M. Brookhart, Thesis, UCLA, 1968; c) A value of 14.7 kcal/mole is calculated for the dimethoxymethyl carbonium ion (in trifluoroacetic acid) from the data of Taft and Ramsey [B. G. Ramsey and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 3058 (1966)].

8. a) A. Nickon and Y. Lin, *J. Amer. Chem. Soc.*, **91**, 6861 (1969); b) A. Nickon and Y. Lin, personal communication.

9. The large upfield shift of the proton in protonated 7-norbornenone relative to that in protonated 7-norbornanone[10] indicates that the former experiences a delocalization of charge. However, the chemical shift[11] and splitting pattern[12] of the vinyl protons suggest that charge delocalization and rehybridization of the trigonal C_7 center is small relative to other less stabilized ions.

10. M. Brookhart, G. C. Levy and S. Winstein, *ibid.*, **89**, 1735 (1967).

11. H. G. Richey, Jr. and R. K. Lustgarten, *ibid.*, **88**, 3136 (1966).

12. M. Brookhart, unpublished observations.

13. R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6350 (1967).

14. R. K. Lustgarten, unpublished observation.