Table I. X-Ray and Optical Crystallographic Properties

$3KF \cdot UF_3$[a]	$3KF \cdot UF_4$[b]	$3KF \cdot UF_5$[c]	$3KF \cdot PaF_5$[d]
Cubic	Cubic	Cubic	fcc
$a_0 = 9.2$ A	$a_0 = 9.2$ A	$a_0 = 9.2$ A	$a_0 = 9.2$ A
1.44[e]	1.436[e]		
Purple–brown	Green		

[a] This work. [b] References 11–13a. [c] Reference 7. [d] Reference 5. [e] Refractive index.

R. E. Thoma, H. A. Friedman
Reactor Chemistry Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee

R. A. Penneman
Los Alamos Scientific Laboratory, University of California
Los Alamos, New Mexico

Received Febuary 14, 1966

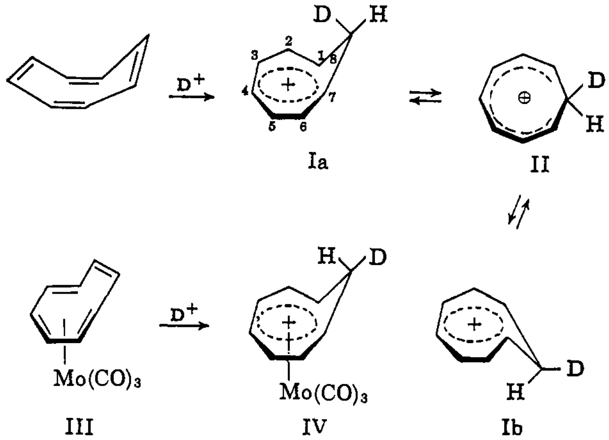
Ring Inversion, Ultraviolet Spectrum, and Electronic Structure of the Monohomotropylium Ion[1,2]

Sir:

The nmr spectrum of the $C_8H_9^+$ ion from protonation of cyclooctatetraene points clearly to the homoaromatic monohomotropylium structure I for this species.[3] This is true also of its molybdenum tricarbonyl complex IV.[3b] We now report on the rate of ring inversion in the monohomotropylium ion and the free-energy difference between this nonclassical species and a classical cyclooctatrienyl cation II. Further insight into the nature of I is provided by its ultraviolet spectrum in comparison with that of tropylium ion V.

Whereas protonation of cyclooctatetraenemolybdenum tricarbonyl (III) in D_2SO_4 is stereospecific,[3b] protonation of cyclooctatetraene (C_8H_8) appeared from earlier reports[3] not to be so. Solutions of C_8H_8 in D_2SO_4 showed *ca.* equal signals for "inside" and "outside" protons,[3a] and the sharpness of these signals made it evident[3b] that *k* for exchange of magnetic environments between these protons is less than 5 sec^{-1}.

When C_8H_8 is dissolved in D_2SO_4 at lower temperatures (−10°) and the nmr spectrum of the solution observed sooner than in the previous work, considerable tendency toward stereospecificity in the protonation step is evident, since about 80% of the incoming deuterium is "inside" (Ia). Thus, the stereospecificity is in the opposite direction from that in the protonation[3b] of C_8H_8–$Mo(CO)_3$ or the CO-evolving protonation[4,5] of C_8H_8–$Mo(CO)_4$. As the observation of the solution of C_8H_8 in D_2SO_4 is continued, the intensities of the inside and outside proton signals approach the value corresponding to half a proton in each position, thus permitting the evaluation of a first-order rate constant for the Ia → Ib isomerization. This is 9.8 × 10^{-4} sec^{-1} at *ca.* 37° and 6.1 × 10^{-4} sec^{-1} at *ca.* 32°, corresponding to a ΔF^* of 22.3 kcal/mole. If the Ia → Ib equilibration is visualized to proceed by ring inversion through a planar form, that of the classical cyclooctatrienyl cation (II), then the free energy of II is shown to be 22.3 kcal/mole higher than that of the homoaromatic monohomotropylium ion (I).



Solutions of C_8H_8 in H_2SO_4 display a reproducible ultraviolet spectrum[6] resembling that of tropylium ion. The two λ_{max} values, 232.5 mμ (log ϵ 4.52) and 313 mμ (log ϵ 3.48), are at higher wavelengths than those for tropylium ion,[7] 217 mμ (log ϵ 4.61) and 273.5 mμ (log ϵ 3.63). Very illuminating is the fact that the λ_{max} for ultraviolet absorption of the homotropylium species I resembles more closely the value for tropylium ion V, with an HMO excitation energy of 1.692β, than the value to be expected for a classical planar cyclooctatrienyl species II with negligible 1,7 interaction. The HMO excitation energy for such an ion is 0.765β, and Deno[8a] has reported λ_{max} at 470 mμ for an actual heptatrienyl cation which could be taken as a model for II.

An estimate can be made of the value of the 1,7-resonance integral (β_{17}) in the homotropylium ion from the position of the long-wavelength ultraviolet absorption maximum at 313 mμ. It has been demonstrated that, for a large number of carbonium ions, a reasonably good correlation exists between the HMO excitation energy and the frequency of long-wavelength absorption.[9] In order that homotropylium fit such a correlation which includes Streitwieser's cations and five additional cations, allylic,[8a] pentadienyl,[8a] benzenium,[8b] and heptatrienyl[8a] in type, its HMO excitation energy must be approximately $1.45\beta_0$ which corresponds to $\beta_{17} = 0.73\beta_0$.[10,11] With this β_{17}, the 1,7 bond order is given as 0.56 by the HMO treatment, compared to 0.69, 0.62, and 0.65 for the π-electron 1,2, 2,3, and 3,4 bond orders, respectively. This is to be compared with a π bond order of 0.64 in tropylium ion.

The tropylium-like electronic description of the monohomotropylium ion (I), with a relatively even electron distribution around the C_1–C_7 carbon atom framework, is in good accord with the general features

---

(1) Reported in part at the Kekulé Celebration Meeting of the German Chemical Society, Bonn, Germany, Sept 14, 1965.

(2) Research sponsored by U. S. Army Research Office (Durham).

(3) (a) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962); (b) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965).

(4) H. D. Kaesz, S. Winstein, and C. G. Kreiter, *ibid.*, **88**, 1319 (1966).

(5) The mechanistic implications of these contrasting stereospecificities are being studied and they will be discussed elsewhere.

(6) The C_8H_8 may be dissolved in H_2SO_4 directly or extracted from a diluted solution of C_8H_8 in CH_2Cl_2.

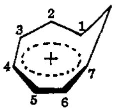
(7) H. J. Dauben, Jr., F. A. Gadeiki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

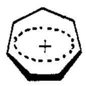
(8) (a) N. C. Deno, *et al.*, *J. Am. Chem. Soc.*, **87**, 2153 (1965); **86**, 1871 (1964); **84**, 1498 (1962); (b) W. von E. Doering, *et al.*, *Tetrahedron*, **4**, 178 (1958).

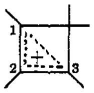
(9) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 228.

(10) In this treatment the normal β_0 is assumed for β_{12}, etc., no allowance being made for the decrease in the corresponding overlap introduced as the conformation of the eight-membered ring in II becomes nonplanar and the 1,7 interaction is thus markedly increased.

(11) A similar procedure has been employed by Katz in estimating a β_{13} of $0.33\beta_0$ in the monohomocyclopropenyl cation VI: T. J. Katz and E. H. Gold, *J. Am. Chem. Soc.*, **86**, 1600 (1964).







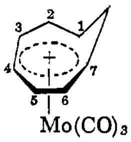
	I	V	VI
λ_{max}, mμ	232.5, 313	217, 273.5[7]	
log ε	4.52, 3.48	4.61, 3.63[7]	
H_{2-6}, τ	1.5[3]	1.0[12]	

of the nmr spectrum of I. Thus, the chemical shift of protons H_{2-6} in I is very similar to the value for H_{1-7} in tropylium ion.[12,13] Further, the chemical shift between "inside" and "outside" C_8 protons in the monohomotropylium ion is well accounted for by a ring-current model using a 1.6-A ring radius and a six-electron induced ring current. Using Framework Molecular Models[14a] to estimate distances and the equation of Johnson and Bovey[14b] to calculate chemical shifts due to induced ring currents, one obtains 5–6 ppm for the difference between inside and outside C_8 protons. This agrees well with the observed[3] difference of 5.8 ppm.[15]

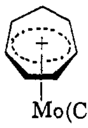
---

[12] H. J. Dauben, private communication: L. R. Honnen, Ph.D. Thesis, University of Washington, 1962; chemical shifts are in H_2SO_4 solvent.

[13] The same similarity of nmr chemical shifts of H_{2-6} in I and H_{1-7} in V is observed also with the corresponding $Mo(CO)_3$ complexes.



$H_{2\text{-}b}$, τ 3.8[3b]



4.3[12]

[14] (a) Framework Molecular Orbital Models, Prentice Hall, Inc., Englewood Cliffs, N. J.; (b) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[15] Note Added in Proof. Just as the present manuscript was submitted, two pertinent communications by C. E. Keller and R. Pettit appeared (*J. Am. Chem. Soc.*, **88**, 604, 606 (1966)). In the first one, these authors report coupling constants for $C_8H_9^+$ essentially identical with those we reported earlier.[3b] Also, they report that the protonation of methyl- and phenylcyclooctatetraene is structurally specific, the 1-substituted monohomotropylium ions being generated. As regards stereospecificity of these protonations in D_2SO_4, these authors observed stereospecificity identical in direction and similar in magnitude with that we report here for the unsubstituted $C_8H_9^+$. For this latter protonation of the unsubstituted cyclooctatetraene in D_2SO_4, Keller and Pettit still refer to the older report[3a] of nonstereospecific protonation, apparently still unaware of the "inside–outside" equilibration. This may be an indication that such equilibration is slower with the substituted ions than with $C_8H_9^+$ itself.

In the second communication, Keller and Pettit object, as we did previously,[3b] to Deno's representation of the monohomotropylium ion with a conventional cyclopropane ring (N. C. Deno, *Progr. Phys. Org. Chem.*, 2, 148 (1964)). They also deal further with the question of a ring current in $C_8H_9^+$. For a series of related structures, with relatively constant geometry, in which the chemical shifts (δ) of the "inside" and "outside" protons vary only because of ring currents, one predicts from the Johnson–Bovey equation[14b] that δ of the inside proton and δ of the outside one should each vary linearly with the chemical shift difference (Δ) between the two protons, Δ being a measure of the magnitude of the ring current. For seven systems plotted this way, roughly linear plots were observed for inside δ *vs.* Δ and outside δ *vs.* Δ. However, these roughly linear plots are fortuitous and misleading, since ring currents are not the only factor causing variation in δ. Variation of the charge at C_8 is also an important factor.

S. Winstein, C. G. Kreiter
Department of Chemistry, University of California
Los Angeles, California 90024

J. I. Brauman
Department of Chemistry, Stanford University
Stanford, California

Received February 14, 1966

Cholesteryl Perchlorate from Carbonium Perchlorate Ion-Pair Return[1,2]

Sir:

In the course of further examination of the $HClO_4$-catalyzed isomerization of *i*-cholesteryl acetate[3a] I (*i*-ROAc) in acetic acid solvent to the thermodynamically favored cholesteryl isomer II (ROAc), we have observed a very instructive example of ion-pair return involving carbonium perchlorate ion pairs. This is described and discussed in the present communication.

The kinetics of the $HClO_4$-catalyzed isomerization of *i*-ROAc to ROAc, followed polarimetrically, do not obey eq 1 for a reaction first order in added $HClO_4$ ($\Sigma HClO_4$), and also first order in *i*-ROAc. As illustrated in Table I, the k_2 values drift upwards badly in each run and vary widely from run to run. While the isomerization is indeed first order in $\Sigma HClO_4$, it appears to be zero order[4] in *i*-ROAc, eq 2 providing a good fit of all the data (Table I).

Table I. Summary of Kinetic Results at 25.0°

(*i*-ROAc), 10^2M	($\Sigma HClO_4$), 10^4M	k_2, l. mole^{-1} sec^{-1}	10^2k_1, sec^{-1}
1.99	0.44	3.7–4.1	2.9
2.00	1.19	1.5–3.4	3.0
2.05	3.36	1.4–3.7	2.9
2.02	4.48	1.4–4.0	2.9
0.51	1.19	6.9–15.2	2.8
0.96	1.19	2.1–11.3	2.9
2.00	1.19	1.5–3.4	3.0
2.67	1.19	0.6–2.7	3.0

$$\text{rate} = k_2(i\text{-ROAc})(\Sigma HClO_4) \quad (1)$$

$$\text{rate} = k_1(\Sigma HClO_4) \quad (2)$$

The explanation which occurred to us for the peculiar kinetics of isomerization of excess *i*-ROAc by $HClO_4$ is that these two materials tend to be in steady-state equilibrium with a covalent perchlorate, chiefly cholesteryl perchlorate (IV, $ROClO_3$), during the isomerization (eq 3–5). This keeps the prevailing $HClO_4$ concentration during a kinetic run down to a small fraction of the added $\Sigma HClO_4$ and inversely proportional to the (*i*-ROAc), while ($ROClO_3$) is essentially equal to ($\Sigma HClO_4$). The kinetics of isomerization of *i*-ROAc are formulated with the aid of the carbonium perchlorate ion pairs[5] III which are formed from *i*-ROAc and undissociated $HClO_4$ (rate constant k_i) and from

---

[1] This research was supported by the National Science Foundation and sponsored by the U. S. Army Research Office (Durham).

[2] Reported in part at the Third Caribbean Chemical Symposium, Caracas, Venezuela, Jan 4–9, 1965 [*Acta Cient. Venezolana*, **15**, 244 (1965)], and the Japanese–American Seminar in Physical-Organic Chemistry, Kyoto, Japan, April 6–10, 1965.

[3] (a) S. Winstein and E. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959); (b) G. H. Whitham and J. A. F. Wickramasinghe, *J. Chem. Soc.*, 1655 (1964); (c) J. H. Beynon, I. M. Heilbron, and F. S. Spring, *ibid.*, 907 (1936); (d) R. Sneen and A. Ehret, unpublished work.

[4] We are indebted to Professor William Dauben, who first called our attention to the superiority of a zero-order plot for this isomerization.

[5] This representation is employed for simplicity, and no implications are intended as regards exact electronic structure[3a,b] of R^+ and the variety of ion pairs[6] involved.

[6] *E.g.*, S. Winstein, P. E. Klinedinst, and G. C. Robinson, *J. Am. Chem. Soc.*, **83**, 885 (1961).