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THE STRUCTURE AND STABILITY OF COATES' CATIONS[1]

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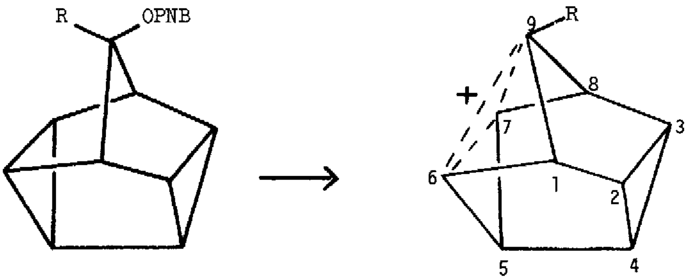
In the course of a theoretical study of trishomocyclopropenium ions,[2] we became interested in the novel, pentacyclic member of this class, **1** (Coates' cation), and its 9-methyl derivative (**2**).[3,4]

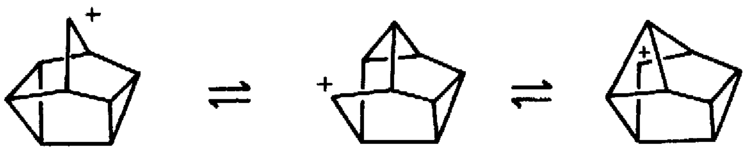


1: R=H

2: R=CH_3

The evidence for **1** as a highly stable, delocalized, nonclassical carbonium ion is undeniable. The key facts are: the rate enhancement of 10^{10}- 10^{12} in the solvolysis of the ester precursor of **1** as compared with 7-norbornyl analogs; complete deuterium scrambling between C9, C6 and C7 in **1**; retention of configuration at C9 upon quenching of **1**; and direct observation of **1** by NMR in superacid at low temperature.[3,4] Furthermore, it should be noted that the rate enhancement cannot be reasonably explained by a set of rapidly equilibrating classical ions because these species are all identical and structurally comparable to a 7-norbornyl cation.[3]

3



Extensive MINDO/3[5] calculations have been performed to help elucidate detailed structures, stabilities and bridge flipping barriers[4] for **1** and **2**. The ability to reproduce the experimental bridge flipping barrier in **2** is an important test of the MINDO/3 method's capacity to represent trishomocyclopropenyl cations.

Structures and Barriers

1 is calculated to possess C_{3V} symmetry: the C_3 axis passes through the centers of the C2C3C4, C1C5C8 and C6C7C9 triangles. This is consistent with the NMR data[4] which indicate three sets of three equivalent carbons and with expectation based on the structure of the parent trishomocyclopropenyl cation.[2] Assuming C_{2V} symmetry (3) for the transition state, the bridge flipping barrier for 1 is computed to be 22.1 kcal/mole. An experimental reference is not available in this case.[4] The calculated CC bond lengths and charges for 1 and 3 are recorded in Table I.

Table I. Calculated Bond Lengths and Charges

R(Å)	1(C_{3V})	3(C_{2V})	q	1(C_{3V})	3(C_{2V})
C6C9	1.735	2.274	C9	0.105	0.416
C1C2	1.542	1.567	C1	0.016	-0.009
C1C6	1.536	1.567	C2	0.002	-0.011
C2C3	1.544	1.554	C4		0.038
C2C4		1.536			
C1C9		1.495			
C4C5		1.527			

The agreement between the MINDO/3 value for the bridge flipping barrier in 2 (8.8 kcal/mole) and the experimental value (13.0 kcal/mole) is good.[2] The transition state (4) was assumed to possess C_{2V} symmetry for the cyclic framework (cf., 3) and C_S symmetry for the methyl group. Overall, the barriers in 1 and 2 are comparable to the experimental values for those in the 7-norbornadienyl cation (≥ 19.6 kcal/mole) and its 7-methyl derivative (12.4 kcal/mole).[7]

Charge Distributions and Stabilities

The source of the reduction in the bridge flipping barrier upon methyl substitution may be traced to selective stabilization of the transition state (4) for the flipping in 2. This is apparent in the calculated ΔH's for the isodesmic reactions given by eqs. 1 and 2. The lack of stabilization of 1 by methyl substitution (eq. 1) can be attributed to the remarkable charge delocalization in 1 (Table I). This portends small substituent effects on solvolyses leading to derivatives of 1.[8]

(1) $2 + C_2H_6 \longrightarrow 1 + CH_3CH_2CH_3 \quad \Delta H = -1.8$ kcal/mole

(2) $4 + C_2H_6 \longrightarrow 3 + CH_3CH_2CH_3 \quad \Delta H = 11.5$ kcal/mole

5

The charge delocalization in 1 is significantly greater than in the parent trishomocyclopropenyl cation (5)[2] which has q(C1)=0.120. The origin of the stabilizing charge shift is uncovered by an analysis of the frontier orbitals of 1. The important component orbitals that must be considered are shown schematically in Fig. 1 with the appropriate labels for C_{3V} symmetry.[9] In C_{3V} symmetry all orbitals are in the A_1, A_2 or degenerate E (E_S or E_A) representations. The A_1, E_S* and E_A* orbitals are the triad for the three equivalent orbitals taking part in the two-electron, three-center bond in the trishomocyclopropenyl fragment. A_1 is occupied by two electrons, while E_S* and E_A* are the principal components in the degenerate LUMO's for 1. The a_1, e_s and e_a orbitals are the fimiliar, occupied Walsh orbitals of a cyclopropane ring.[9] The three occupied bond orbitals of the C1C2, C3C8 and C4C5 bonds form an analogous trio. Only the E_S and E_A pair have been shown in this case. The A_1 combination is at low energy and will not be

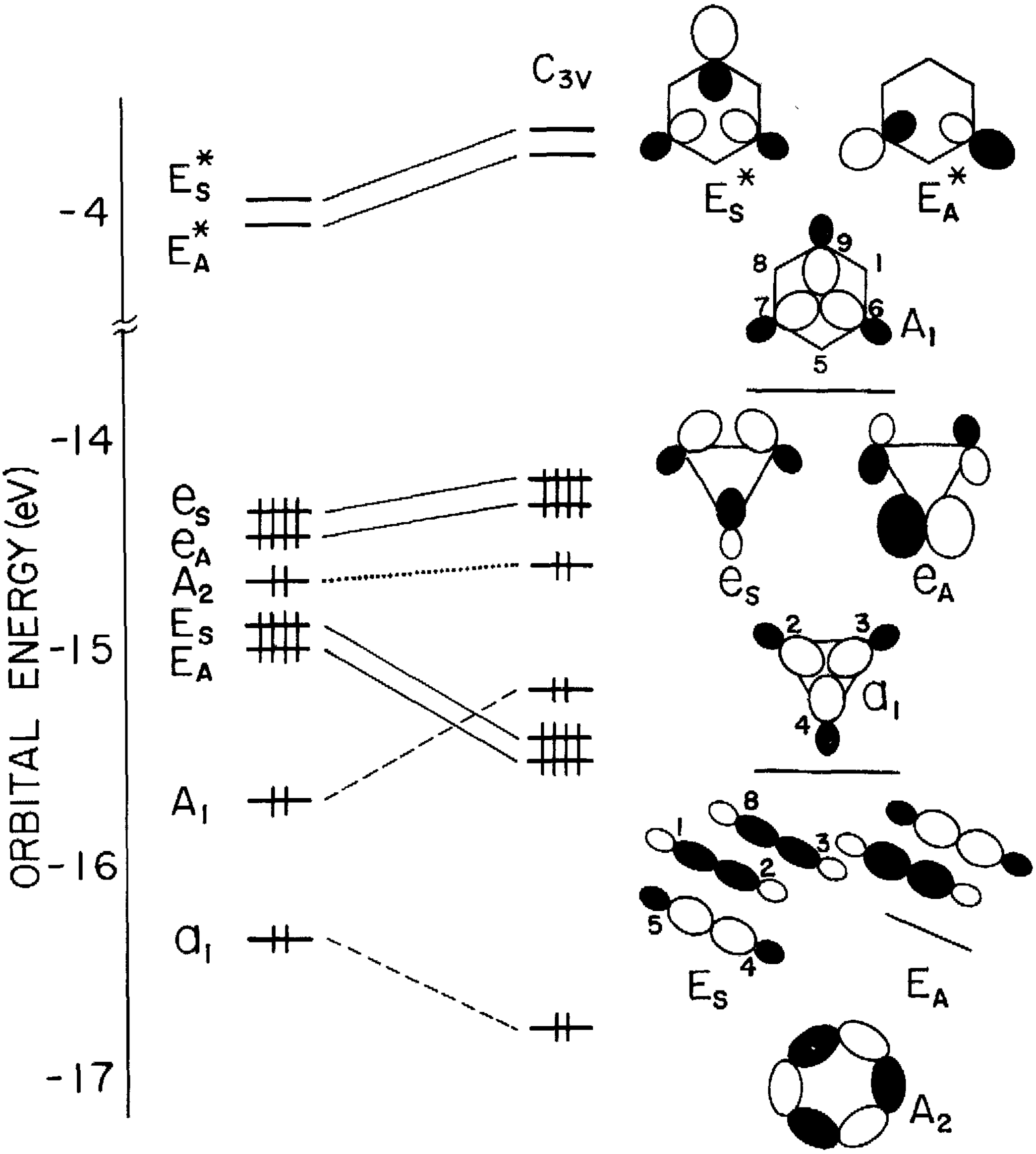


Figure 1. Frontier orbitals and their interactions in **1**.

considered. Finally, the A_2 orbital is the highest-lying, occupied combination of bond orbitals for the trishomocyclopropenyl ring.

A rough ordering of the localized orbitals is given in the left column of Fig. 1. When the orbitals of like symmetry interact, delocalized orbitals are formed as indicated. The final orbital energies and ordering are the MINDO/3 results. An EH calculation yields an identical ordering except with A_2 as the HOMO. Note that the HOMO's in **1** are centered on the cyclopropyl ring and adjacent bonds, while the LUMO's are localized on the most electron deficient carbons. When the component orbitals interact, the principal electron donation is expected from the HOMO's with E symmetry to the LUMO's.[9] Thus, for **1** this corresponds to enhanced delocalization of the positive charge from the electron deficient carbons to the rest of the molecule. There is less charge delocalization in **5** because the high-lying, component orbitals with E symmetry are absent. Instead, the HOMO of **5** is A_1.

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