Tetrahedron. Vol. 30, pp. 1393 to 1395. Pergamon Press 1974. Printed in Great Britain

THE GEOMETRY OF GOLDSTEIN AND KLINE'S $C_{11}H_{11}$ CATION

C. TRINDLE,[1a]* JENN-TAI HWANG[1b] and D. HOUGH
Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

(*Received in the USA* 21 *November* 1973; *Received in the UK for publication* 23 *January* (1974)

Abstract—Semi-empirical computations on the $C_{11}H_{11}$ cation reported by Goldstein and Kline[2] indicate that a classical structure suggested by models is not an appropriate representation of the system. A system with C_s symmetry differing in detail from the "quasi D_{2d}" form proposed by the discoverers is found to be the stable form. The reasons for easy rearrangement in this system are discussed.

The magnetic resonance spectrum of a polycyclic $C_{11}H_{11}$ cation has been reported by Goldstein and Kline.[2] The system displays a 5-fold equivalence among protons at centers 1, 2, ... 5, 4-fold equivalence among protons at centers 6, 8, 9, and 11, and equivalence among protons at centers 7 and 10 (Fig 1). The equivalences suggest a sequence of rapid rearrangements which may be represented by powers of the permutation-inversion (11 8 9 6) (7 10) (3 2 1 5 4).* The set of powers of this operator form a Longuet-Higgins group,[3] which has been used to classify states of the rapidly rearranging cations.[4] However, one question which the group theory is powerless to answer is the detailed structure of the static species. The purpose of this report is to present approximate MO computations on the $C_{11}H_{11}$ cation, designed to distinguish between the classical structure one might obtain by model building and nonclassical structures such as the quasi-D_{2d} form proposed by Goldstein and Kline.

Our computational model is the familiar CNDO method developed by Pople *et al.*[5] The novel feature of the computation is the means by which the geometric parameters are varied. One of us (J.-T. H.) has developed a program which computes Cartesian coordinates given bond lengths and bond angles, torsion angles and dihedral angles.[6] In contrast with many extant programs of similar intent, this program can distort and pucker ring systems arbitrarily while guaranteeing that the rings remain closed. Details or a full listing of the program may be obtained from C. T.

In a system of the size of $C_{11}H_{11}^+$, it is required that only a small number of variables be explored. Of course serious errors can attend fixing a majority of the geometric parameters, and it is necessary to examine the choices with some care. Our major assumptions deal with bond lengths: all CH bonds are assigned a length of 1·1 Å, and all CC bonds in the 5-membered ring are assigned the length 1·5 Å. In the first sequence of computations, which was intended to generate the best classical structure, the CC bonds in the formally charged allyl fragment, below the ring were fixed at 1·4 Å, while the 7–8 "double bond" above the plane was set to 1·3 Å, while its neighboring single bond was set to 1·5 Å. All CC bonds connecting allyl fragments to the ring were assigned 1·5 Å lengths. A plane of symmetry is maintained through the variation. Modifications to these assignments were made in a second series of computations, which will be described below.

The variables altered in our search for a classical $C_{11}H_{11}^+$ species are made explicit in Fig 1b. The dihedral angle between the 2–9–10–11–4 ring (assumed planar due to the three sp^2 carbons in the allyl fragment), and the 2–1–5–4 plane, and the distance from 10 to the 2–4 midpoint fix the lower ring. The 6–8 distance, which specifies the arrangement of the upper allyl fragment assuming a 6–7–8 angle of 120° and a 5-membered ring fixed by other variables was varied. Puckering the 5-membered ring is permitted by altering the 3–7 distance

The computed classical structure (Fig 1c) requires only slight (~ 20°) puckering of the 5-membered ring, but shows a large dihedral angle (~ 120°) between the 2–9–10–11–4 plane and the 2–3–4 fragment of the ring.

This species does not resemble the "sandwich compound" proposed by Goldstein and Klein, though its structure suggests that establishment of a bonding interaction between 9 and 1 (or 11 and 5) at the expense of the 6–1 (or 6–5) bond will not be very difficult. The 9–1 distance is only 1·77 Å, so a vigorous vibration along the 9–1 vector could set off the rearrangement in which the 1–2–9 ring would be formed.

In order to give Goldstein and Kline's proposal of a pi-sandwich a fairer test, we began another series of computations from a D_{2h} arrangement of allyl D_{2d}

fragments with CC distance of 1·4 Å. The allyl–allyl D_{2d} axis was chosen to pass through the centroid of a regular pentagonal C_5H_5 with R_{CC} = 1·5 Å placed at the axis' bisector. The altitude of C_7 (assumed equal to the depth of C_{10}) from the pentagon was optimized, and we found that this regular arrangement was more stable than the best classical species. This seemed to be strong support for Goldstein and Kline's proposal; however, departures from this structure stabilize the system still further. First rotation of the top allyl fragment in the plane of symmetry is favored, so that the 3–8 distance was increased to *ca* 1·5 Å and the 6-8 distance was decreased to *ca* 1·3 Å. This motion makes the 3–8 bond and the 1–6–5 bonds become essentially classical. This motion is small; the 6–7–8 bisector departs from the original "D_2" axis by *ca* 5°.

The 9–10–11 bisector was displaced in the plane of symmetry, while the separation between 10 and the plane was altered. We found that the 2–9 and 4–11 distances became 1·5 Å, a classical CC bond distance, and the dihedral angle between the 2–9–11–4 plane and the 5-membered ring approached 60°, just as in the classical model. To our momentary surprise, forcing the 2–9–10–11–4 to be planar is opposed by a considerable energy, roughly 0·05 CNDO units (nominally atomic units). In view of this, and the fact that the 9–1 and 11–5 distances are less than 1·6 Å in the optimized structure (i.e., 1–2–9 is almost isosceles) we prefer to describe the 1–2–9 arrangement as a highly asymmetric 3-center bond which becomes symmetric as the rearrangement proceeds. Bond indices[7] for the several CC bonds summarized in the table show that the CC bonds in the 3-membered ring 1–5–6 are weak, while there is a substantial 1–9 interaction, 50% of a full bond. The lower allyl fragment shows no pi bonding worth quoting, so the representation of the three carbon 9–10–11 fragment as an allyl group is certainly mistaken. The upper 6–7–8 fragment is dominated by the 6–7 single bond, 7–8 double bond VB structure, since the 6–7 pi interaction involves only 0·145 electron pairs while the 7–8 pi interaction involves 0·75 electron pairs according to the Wiberg bond index.[7] It is worth noting the weakness of the 1–6 and 5–6 bonds, involving only 0·75 electron pairs, and the strength of the (nominally nonbonding) interactions between 1 and 9 and 5 and 11, which involve 0·51 electron pairs. The 1–9 distance in the optimized structure is only 1·56 Å. This structure purports to represent carbons 1 and 5 as suffering five substantial interactions, a situation typical of transition states. We are not surprised than that a rearrangement which "breaks" the 1–6 bond and "makes" the 9–1 bond should be easy, since the bond indices are in fact shifting only slightly: the CC motion is within a normal vibrational amplitude.

The ease of the rearrangement is further emphasized by an analysis of the orbital structure in the manner of Salem and Wright.[8] There is a low-lying, unoccupied orbital, nominally bound at −0·15 a.u.: the HOMO lies at −0·44 a.u. and the next highest unoccupied orbital lies at −0·02 a.u. Clearly the LUMO will dominate the perturbation theoretic analysis of easy motions. The HOMO-LUMO transition density is large and directed in the

Table. Bond lengths[a] and indices[7]

1–5	1·5[b]	0·855
1–6	1·5	0·746
1–2	1·5[b]	0·740
2–3	1·5[b]	0·940
6–7	1·4[b]	0·992/0·145[c]
7–8	1·4[b]	0·999/0·750[c]
2–9	1·5	0 940
9–10	1·4[b]	0·995/0·022[c]
1...9	1·56	0·509
3–8	1·5	0·968

[a] in Ångstroms
[b] assumed: not optimized
[c] sigma/pi

Angles 6–7–8 and 9–10–11 assumed 120°.

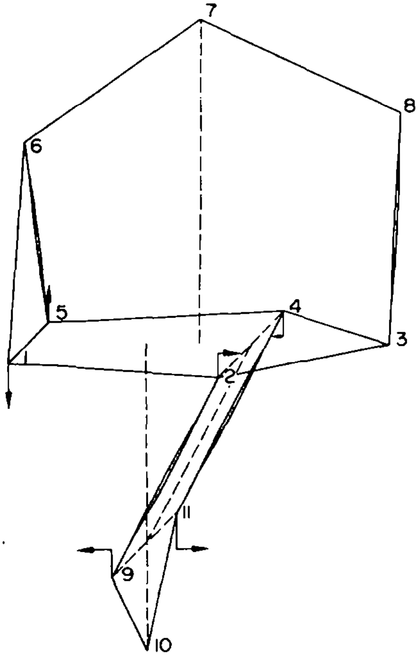

Fig 1a. The computed optimum structure for $C_{11}H_{11}$ cation. The 9-10-11 and 6-7-8 planes are orthogonal and the five-membered ring is planar, as Goldstein and Kline propose. However, the D_{2h} arrangement of the two three-carbon fragments does not obtain. There is an asymmetric 3-center bond at 1-2-9 and 5-4-11, and the 1-6 and 5-6 bonds are weak (see text). E = −89·763 a.u. or −56323 kcal/mole.

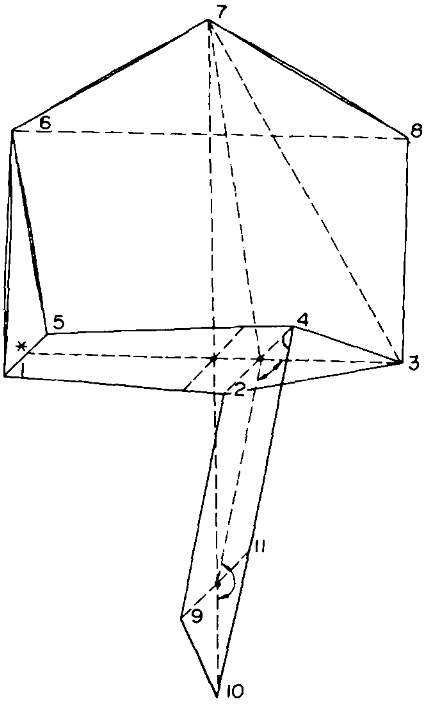

Fig 1b. The variables altered in the course of the computation are shown: for discussion, see text.

manner indicated by arrows in Fig 1a. The maximum second-order stabilization will occur when the system distorts along the arrows. This motion closes the 1–9 bond at the expense of the 1–6 bond if the motion is as shown: at the other extreme of the vibration, the 11–5 bond is formed at the expense of the 5–6 bond. These easy motions coincide with the predicted mode of rearrangement.

The asymmetric but inescapable three center bonding in the 1–2–9 and 5–4–11 regions, coupled with the non-allylic nature of the 9–10–11 fragment indicate strongly that the bonding in this system is nonclassical, and that the easy rearrangement if intimately associated with the multi-center bonding. Thus our computations lend support to Goldstein and Kline's suggestion of sandwich-type bonding in $C_{11}H_{11}$ cation, even though we find departures in detail from the proposed structure.

Acknowledgement—This work was made possible by generous grants of computer time from the Division of Academic Computing of the University of Virginia.

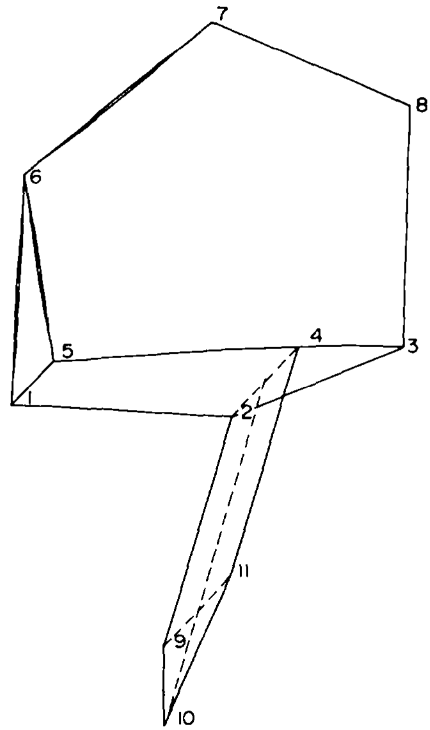

Fig 1c. The optimum "classical" structure, which has a 7-8 double bond and a 6-7 single bond (1·3 and 1·5 Å respectively) and which has an established 9-10-11 allyl fragment forcing 2-9-10-11-4 to be planar, requires a 20° pucker of the five membered ring and has a dihedral angle between the 1-2-4-5 and 2-9-10-11-4 planes which is smaller than models predict. The classical structure is not competitive in energy with the species shown in Fig 1a: E = − 89·422 a.u. or − 56109 kcal/mole.

REFERENCES

[1] [a]To whom correspondence should be directed: A. P. Sloan fellow, 1971–73; [b]present address: Department of Chemistry, Columbia University, New York City, New York

[2] M. J. Goldstein and S. A. Kline, *J. Am. Chem. Soc.* **95**, 935 (1973)

[3] H. C. Longuet-Higgins, *Mol. Phys.* **6**, 445 (1963)

[4] C. Trindle and T. D. Bouman, *Proc. VI Jerusalem Symp.* (Edited by E. D. Bergman and B. A. Pullman) Israel Acad. Sci. Hum. (1973)

[5] J. A. Pople and D. A. Beveridge, *Approximate Molecular Orbital Theory.* McGraw-Hill, (1971)

[6] J. -T. Hwang, *Optimization of Molecular Geometries.* M. S. Thesis, University of Virginia (1973)

[7] K. B. Wiberg, *Tetrahedron* **24**, 1083 (1968); C. Trindle, *J. Am. Chem. Soc.* **91**, 219 (1969)

[8] L. Salem and J. S. Wright, *Ibid.* **91**, 5947 (1969)