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Determination of the Structure of the 1,2,4,7-*anti*-Tetramethyl-2-norbornyl Cation: An AIM Study

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While the *molecular geometry* of the 1,2,4,7-*anti*-tetramethyl-2-norbornyl cation (**1**), as reported previously from a crystal structure analysis, is reproduced nicely at the Becke3LYP/6-31G(d,p) level of theory, the conclusions drawn from that analysis about the *molecular structure* cannot be rationalized. The topology of the charge density of **1** is in keeping with a hyperconjugatively stabilized 2-norbornyl cation; **1** is not bridged and it does not show a 3-center−2-electron bond as had been reported. This was revealed in an atoms in molecules (AIM) study.

Introduction

Molecular structure and molecular geometry are generic and nongeneric properties of a system, respectively. As Bader pointed out,[1] while the terms structure and geometry are often used interchangeably, it is most important to distinguish clearly between them. For a given configuration of a molecule, an infinitesimal change in the nuclear coordinates gives a new geometry, yet the molecule's stable structure, i.e., the network of bonds linking the nuclei called the molecular graph, does not change. Even though a "crystal structure" analysis recovers the distribution of the charge density $\rho(r)$ and the full information offered by the scalar field $\rho(r)$—its topology as given by all its critical points, i.e., points where $\nabla\rho(r)$ is zero—is basically available, usually only nuclear coordinates are determined from it. The relative ease with which the coordinates of non-hydrogen nuclei can be refined arises from the fact that generally $\rho(r)$ is a maximum only at the positions of the nuclei, which behave like (3, −3) critical points[2] and that the magnitude of $\rho(r)$ is determined by the nuclear charge. The value of $\rho(r)$ at the position of a proton being some orders of magnitude smaller than that at the position of a carbon nucleus often leads to problems in the refinement of proton coordinates. But these problems can be overcome and the *molecular geometry* is obtained. The data contained in the rest of $\rho(r)$ are ignored in the routine determination of a "crystal structure". Yet only this −neglected− part of the charge distribution gives information about the *molecular structure*![3] Two nuclei of two atoms we consider bonded are linked to one another by a line of maximum density through space, an atomic interaction line. Such a line is defined by a pair of unique trajectories of $\nabla\rho$ originating at a (3, −1) critical point,[2] a point where the density attains its minimum value along this line.[1] For a geometry at equilibrium, we call the line a bond path and the point a bond critical point.[6] A (3, −1) critical point is the necessary and sufficient criterion for two atoms to be bonded to one another.[1,6] Where chemical intuition tells us to "draw a bond" and where an analysis of the topology of the charge density gives a bond path usually coincide. But there are molecular systems where *only* this latter analysis of the topology of $\rho(r)$ can give the correct bond path—and with the network of the bond paths the molecular graph—and chemical intuition fails.[7] Not surprisingly, it fails in a field that has been the subject of dispute for 50 years, the "nonclassical" cation. In a previous communication, we have shown that, from the topology of its charge density, the C_s-symmetrical 2-norbornyl cation, the "nonclassical" prototype, is best described as a π-complex, a cation interacting with a double bond.[7] While its C_s-symmetrical geometry is undisputed, the cation does not show the topology of $\rho(r)$ associated with a bridged structure, which it was assigned by chemical intuition. In this paper, we (re)evaluate the molecular structure of the 1,2,4,7-*anti*-tetramethyl-2-norbornyl cation (**1**), *which has been reported to possess a bridged structure as determined from its crystal structure*,[5] with the aim of showing that it is important to consider $\rho(r)$ in its entirety.

Computational Details

Becke3LYP[8] calculations were carried out with Gaussian 94[9] on IBM SP2, CRAY T90, and SGI R10000 Impact computers. The molecules were fully optimized with the 6-31G(d,p) basis set (the global minimum of the 2-norbornyl cation was reported previously at this level of theory,[7,10] and an account for this choice was given). The stationary points were characterized as minima through frequency calculations, and the total energies of the cations are corrected for zero-point vibrational energies.

The studies of the electronic charge density $\rho(r)$ and its gradient vector field $\nabla\,\rho(r)$ as well as the integrations (to obtain the net charges)[11] were carried out with the AIMPAC[12] series of programs.[13] In the plots of $\rho(r)$ and $\nabla\rho(r)$, solid crosses indicate positions of nuclei in the plane and open crosses those of nuclei out of plane. The position of a (3, −1) critical point is marked by a black dot. The smallest contour value in the contour plots of $\rho(r)$ is 0.001 au. Ball and cylinder representations are plotted from HyperChem 5.0.[14]

Results and Discussion

The first crystal structure of a purely alkyl-substituted 2-norbornyl cation was reported in 1987 by Laube, who succeeded in crystallizing the Sb_2F_{11} salt of the 1,2,4,7-*anti*-tetramethyl-2-norbornyl cation (**1**).[5a] Laube repeated the analysis

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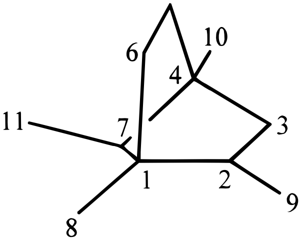
TABLE 1: Properties of C−C Bonds of Cation 1 and Its Neutral Hydrocarbon 1hc[a]: Bond Length r_e (pm), Charge $\rho(r_c)$ (e Å^{-3}), Bond Order n^b, Ellipticity ϵ, and Laplacian $\nabla^2\rho(r_c)$ (e Å^{-5})

	r_e					
	expt[c]	calcd	$\rho(r_c)$	n	ϵ	$\nabla^2\rho(r_c)$
C^1-C^2	140.9(9)	143.4	2.013 (1.582)	1.45 (0.94)	0.09 (0.01)	−19.08 (−12.12)
C^2-C^3	149.1(8)	148.7	1.824 (1.573)	1.20 (0.93)	0.03 (0.01)	−16.25 (−12.15)
C^6-C^1	171.0(8)	170.6	1.088 (1.609)	0.57 (0.97)	0.12 (0.01)	−5.11 (−12.56)
C^6-C^2	211.3(9)[d]	217.8[d]				
C^2-C^9	145.7(8)	147.6	1.828 (1.649)	1.20 (1.01)	0.02 (0.01)	−16.60 (−13.35)

[a] Given in parentheses for $\rho(r_c)$, n, ϵ, and $\nabla^2\rho(r_c)$ of **1hc** with the methyl group on C^2 equatorial (the total energy is −431.254627 au); the diastereomer with this methyl group axial is only marginally higher in energy (−431.254616 au). [b] Determined for this level of theory from $\rho(r_c)^1$ as $n = \exp[\rho(r_c) - 1.642]$. [c] Reference 5b. [d] Internuclear distance, not a bond length.

in 1994 at a lower temperature and got a similar but slightly more precise result (110 K: $R1 = 5.76\%$, 193 K: $R = 8.0\%$).[5b] In a questionable comparison, the skeletal geometry of **1** was shown to be strongly distorted from the calculated geometries of both the neutral, unsubstituted norbornane and the C_s-symmetrical 2-norbornyl cation, but practically identical with that of the unsymmetrical 2-norbornyl cation (which, at higher HF levels, is not a stationary point but is a transition state[15] with Becke3LYP). **1** was labeled "bridged", and dotted lines (or open bonds) were drawn between C^6 and C^2; at the same time, an orbital description explaining stabilization through hyperconjugation in the cation was presented, clearly showing the uncertainty of how to describe the molecular structure.[5] Schleyer and Maerker used the experimental geometry of **1** (as reported in ref 5a) for a comparison with a geometry computed at the Becke3LYP/6-31G(d) level.[16] There is a reasonable agreement between the two sets of data (the agreement is considerably better when the geometry from ref 5b is used), which again shows that the *geometry* can be determined rather accurately. However, their paper with a statement about the "length of the partial bonds associated with nonclassical carbocations" only adds to the confusion of the *structure* issue. But as we have shown before,[7] there is no need for this dilemma, as the necessary information for a structure determination is contained in the molecule's charge distribution and can be extracted and interpreted with the help of the theory of atoms in molecules (AIM).[1] The charge density at the position of a (3, −1) critical point is some orders of magnitude smaller than at the position of a proton, which is why the charge distribution for an AIM study usually is obtained from the wave function of high-level ab intio or density functional calculations. Our results regarding the molecular structures of the 2-norbornyl and the 2-bicyclo[2.2.2]octyl cation already suggest that Becke3LYP/6-31G(d,p) produces wave functions of high accuracy;[7] a comparison of the computed with the available geometrical parameters from ref 5b, given in Table 1, evaluates the quality of this level of theory.[17]



The analysis of the charge density in the crucial region of **1**, i.e., in the $C^6-C^1-C^2$ plane, reveals only two (3, −1) critical points, one between C^1 and C^2 (cp_b1) and the other between C^1 and C^6 (cp_b2) (Figure 1). A bridged structure requires three (3, −1) critical points, the above two and, in addition, one between C^6 and C^2 to form a ring, along with a (3, +1) critical point[2] for the $C^6-C^1-C^2$ ring system; this is not found. Figure 1a is a display of a contour map of $\rho(r)$ for the $C^6-C^1-C^2$ plane with cp_b1 and cp_b2 and their associated trajectories superposed. The trajectories terminating at the nuclei define the part of the molecular graph in question, while those terminating at the two (3, −1) critical points define the boundaries of the three atoms. Figure 1b shows the corresponding gradient vector field of $\rho(r)$. These maps show clearly that the basin of C^1 extends into the space between C^6 and C^2 and that therefore

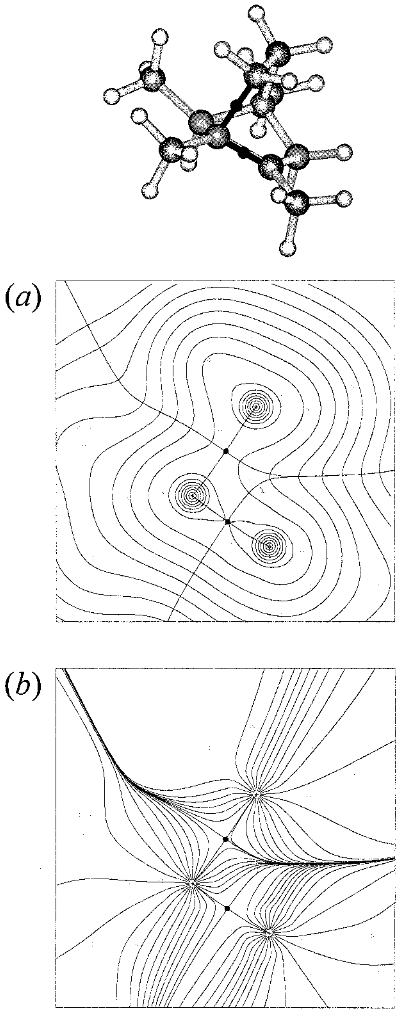


Figure 1. Displays of (a) the contour map of $\rho(r)$ for the $C^6-C^1-C^2$ plane of **1** and (b) the corresponding gradient vector field. Two (3, −1) critical points, shown as black dots, and their associated trajectories are superposed on both maps. The ball and cylinder presentation of the molecule (including the crucial bond paths as thick black lines) gives the orientation.

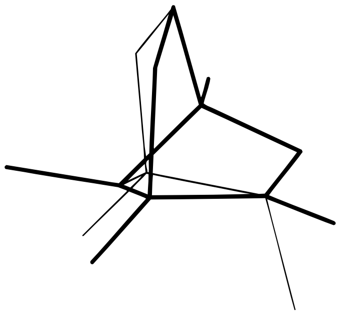


Figure 2. Superposition of the computed carbon skeletons of cation **1** (thick lines) and hydrocarbon **1hc** (thin lines).

the interatomic surfaces of C^6 and C^2 are distinct; there can be no (3, −1) critical point between these two carbon nuclei. And as every structural change, including that from an open to a bridged structure, is abrupt, not continuous,[1] there are no “partially bridged” ions.[5c]

While the above is based on the topology of the charge density, it is consistent with a hyperconjugatively stabilized carbocation in the molecular orbital picture. Contrary to what was said,[5c] there is a clear boundary between bridging and hyperconjugation. And just as the topology of the charge density reveals (3, −1) and (3, +1) critical points of a bridged structure, there are certain “anticipated consequences of hyperconjugation”,[18] which can be tested for with the theory of atoms in molecules. That hyperconjugation is responsible for the stabilization of **1** can be read from the properties—the charge $\rho(r_c)$ (and with it the bond order[1] n), its Laplacian $\nabla^2\rho(r_c)$, and the ellipticity[1] ϵ—of the participating bonds at their (3, −1) critical points[18] as given in Table 1 for C−C bonds. Values for the neutral hydrocarbon **1hc** are given in parentheses for comparison; that the cation is, in fact, very close in geometry to its neutral hydrocarbon, and with that to the “classical” geometry, can be seen from the superposition of **1** and **1hc** in Figure 2. In the cation, the C^1-C^6 bond donates electron density to the vacant p-orbital on C^2 that leads to a decrease in $\rho(r_c)$ (and n) at cp_b2 and an increase in $\rho(r_c)$ (and n) at cp_b1, which shows the partial double bond character of the C^1-C^2 bond in **1**. In accord with this, $\nabla^2\rho(r_c)$, as a measure of the local charge concentration, becomes less negative at cp_b2 and more negative at cp_b1. That the accumulation of charge at cp_b1 is indeed π-type is reflected in the value of ϵ being greater than zero; in the cation, the two negative curvatures of ρ, λ_1 and λ_2, are no longer of the same magnitude ($\epsilon = \lambda_1/\lambda_2 - 1$) and the curvature of smaller magnitude (λ_2) is directed more or less perpendicular to the $C^1-C^2-C^3$ plane. C−H hyperconjugation affects C^2-C^3 and C^2-C^9 accordingly. While all hydrogen atoms acquire positive charge upon ionization of the hydrocarbon (in the cation, out of a calculated total positive charge of $+0.993 \approx +1$, $+0.467$ resides on the hydrogen atoms), a greater extent of electronic charge removal from a hydrogen atom of a properly aligned C−H bond indicates that this bond is interacting hyperconjugatively.[18] This is found for the exo C−H bond on C^3 and the antiperiplanar (with respect to the empty p-orbital) C−H bond on C^9, where the electronic charges lost on the protons are 0.106 and 0.113 au, respectively, compared to 0.080 au for the endo proton on C^3 and 0.077 and 0.086 au for the two remaining methyl protons on C^9 (the net charges on these hydrogen atoms are given in Figure 3). The lowest unoccupied molecular orbital (LUMO) of **1** (Figure 4) gives an accurate graphical description of the C−C and C−H bonds losing electron charge density due to the hyperconjugative mechanism.

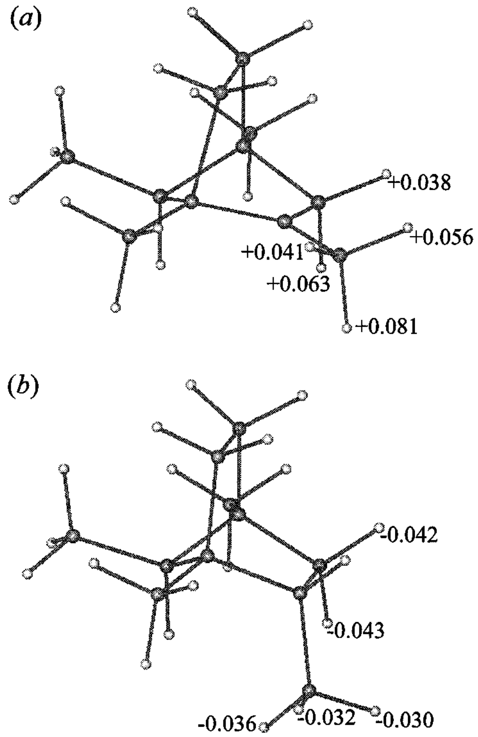


Figure 3. Net charges for selected hydrogen atoms in (a) cation **1** and (b) neutral hydrocarbon **1hc**.

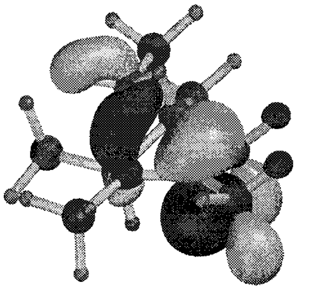


Figure 4. The LUMO of **1** (Becke3LYP/6-31G(d,p)).

Conclusion

Becke3LYP/6-31G(d,p) calculations reproduce the molecular geometry of the 1,2,4,7-*anti*-tetramethyl-2-norbornyl cation (**1**) as it was reported previously from a crystal structure analysis. But the topology of the charge density of **1** shows that it is not bridged and does not show a 3-center−2-electron bond as was also reported. The molecular structure is in keeping with a hyperconjugatively stabilized 2-norbornyl cation. This study shows clearly that it is necessary to consider the full information available from the charge density if the goal is to obtain information about the structure of a molecule.

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(1) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990.

(2) A critical point is labeled by giving the rank ω, the number of nonzero curvatures of ρ, and the signature σ, the algebraic sum of the signs of the curvatures of ρ, as (ω, σ).[1] At a $(3, -3)$ critical point all three curvatures are negative, a $(3, -1)$ or bond critical point possesses two negative and one positive curvature, and at a $(3, +1)$ or ring critical point two curvatures are positive and one is negative.

(3) In the words of a referee, the experiment to determine the crystal structure is routine, while the accurate determination of the electron density using X-ray diffraction is a difficult time-consuming technique. That this is indeed the case has been outlined in several proceedings.[4] With this paper we want to emphasize that the molecular structure can only be determined from a full analysis of the charge density and not from a classical crystal structure experiment as has been done for **1**.[5]

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(17) We found that the isomeric 1,2,3,4-tetramethyl-2-norbornyl cation **1i** is slightly lower in energy (zero-point corrected total energies are -430.105431 au (**1**) and -430.106498 au (**1i**)); the implications of this are under investigation. The results of the structural analysis for **1** apply to **1i** as well.

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