Protonated 1,3,4,5-Tetramethylbicyclo[3.1.0]hex-3-en-2-one Hexachloroantimonate[1]

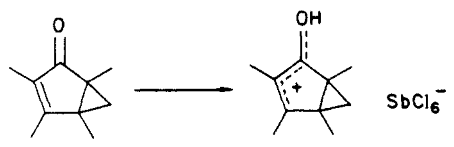
Satish K. Chadda, Ronald F. Childs,* Romolo Faggiani, and Colin J. L. Lock

Department of Chemistry, McMaster University
Hamilton, Ontario, Canada L8S 4M1

Received November 25, 1985

In seeking to define the structural consequences of homoaromaticity,[2] it is instructive to examine the structure of a nonaromatic cation. The bicyclo[3.1.0]hexenyl cations are a case in point, in which involvement of the internal cyclopropane bond in cyclic electron delocalization would lead to a $4n\pi$ electron system. There are many reported investigations of these nonaromatic cations,[3] however, we report here the first structure determination.

Most bicyclo[3.1.0]hexenyl cations readily isomerize to the corresponding benzenium ions and this renders the isolation and crystallization of these ions difficult. Placement of a hydroxy group on the five-membered ring greatly enhances their kinetic stability and for this reason we chose to work with these derivatives. Treatment of **1** with HCl/$SbCl_5$ led to the formation of **2** which could be isolated as crystalline solid. The ^1H NMR spectrum of **2** in CH_2Cl_2, which was very similar to those obtained for solutions of **1** in strong acids,[4] was typical of a bicyclohexenyl cation.[3]



1 **2**

The struture of **2**, determined using X-ray diffraction, is shown in Figure 1, and important internuclear distances and angles are summarized in Table I. During the structure determination, it became apparent that a molecule of water had been incorporated into the crystal lattice in a position to accept a hydrogen bond from the proton on the carbonyl group (O,O distance 2.550 Å). From our other work on the structures of protonated carbonyl compounds it is clear that the proton on a carbonyl oxygen is acidic and always hydrogen-bonded to a Lewis base in the lattice.[5] Similar H bonding undoubtedly also occurs in solutions of protonated carbonyl compounds and this interaction should not perturb the structure of the cation in this present case. All attempts to prepare a crystalline sample without this water have proved to be unsuccessful to this point.

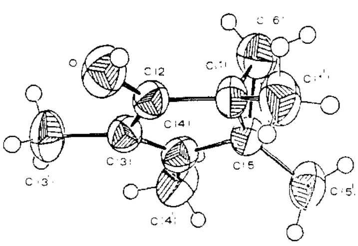


Figure 1. Structure **2**.

The internuclear distances of the protonated enone fragment of **2** are very similar to those found for other related structures.[6] The C,O bond (1.280 (6) Å) is elongated as compared to a neutral carbonyl and there has been a contraction of the C_2,C_3 bond and lengthening of the C_3,C_4 bond, as compared to a corresponding neutral system.[7] It is clear from these features of the structure of **2** that we are dealing with a protonated carbonyl compound and that the proton is not bound to the water molecule and simply hydrogen bonded to the carbonyl oxygen. This is expected since water is a significantly weaker base than most carbonyl compounds.[8]

The bond distances found in the cyclopropyl ring of **2** are of particular interest. Two of the distances, C_1,C_5 and C_5,C_6, are the same as that of a regular cyclopropyl ring whereas the external bond C_1,C_6 is longer than would be expected. This pattern of bond distances is quite different from that observed for a cyclopropylcarbinyl cation,[9] and clearly a different type of electron delocalization is occurring.

The cyclopropyl ring in **2** differs in conformation and substituent pattern from the cyclopropyl carbinyl cations presented in the previous paper. First, the cyclopropyl ring adopts a trans gauche conformation in **2**. This would be expected to make the two vicinal bonds nonequivalent in terms of participation with the positively charged center. Second, the cyclopropyl ring in **2** has two π-type electron-withdrawing substituents and this would normally be expected to lead to an elongation of the cyclopropyl bond which is vicinal to both substituents.[10] This effect is well demonstrated in the very long internal cyclopropyl bond (1.626 (8) Å) found in protonated 2,3-homotropone, **3**, in which the cyclopropyl ring is in a similar position with respect to the protonated carbonyl and vinyl groups.[2] In the case of **2**, however, the C_1, C_5 bond (1.511 (7) Å) is no longer than that normally found for a cyclopropyl bond, and this would clearly point to the fundamental difference in the electron delocalization in **2** as compared to the cyclic, homoaromatic type of delocalization present in **3**. Indeed, this very large structural difference between **2** and **3** fully confirms the designation of the latter system as homoaromatic.

A further point emerges in comparing the structure of **2** with those of other protonated cyclopropyl ketones, namely, the very large difference in the distance between the carbonyl carbon and the cyclopropyl carbon in the two systems. In the three previous structure determinations of protonated cyclopropyl ketones, the average C(O),C bond distance was 1.423 (10) Å, whereas in **2** this distance (C_1,C_2, 1.474 (7) Å) is much greater (difference 4.2σ, $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$). Similarly the C_4,C_5 bond distance in **2** (1.510 (7)) is significantly longer than would be expected in neutral systems for an unsaturated carbon bonded to a cyclopropane (1.465 (3) Å (difference 5.9σ) in bisected and possibly even in

Table I. Selected Interatomic Distances (Å) and Angles (deg)

C(1)-C(2)	1.474 (7)	C(2)-C(3)	1.410 (8)	C(3)-C(4)	1.351 (8)
C(4)-C(5)	1.510 (7)	C(5)-C(6)	1.501 (8)	C(6)-C(1)	1.547 (8)
C(1)-C(5)	1.511 (7)	C(1)-C(1′)	1.493 (8)	C(2)-O	1.280 (6)
C(3)-C(3′)	1.502 (7)	C(4)-C(4′)	1.479 (8)	C(5)-C(5′)	1.500 (8)
		Hydrogen Bonds			
O(2)···O	2.550 (7)	O(2)-H(2)	0.62	H(2)···O	1.96
C(6)-C(1)-C(2)	111.5 (5)	C(1)-C(2)-C(3)	112.0 (5)	C(2)-C(3)-C(4)	108.6 (5)
C(3)-C(4)-C(5)	111.0 (5)	C(4)-C(5)-C(6)	110.5 (5)	C(1)-C(6)-C(5)	59.4 (5)
C(6)-C(1)-C(1′)	120.5 (5)	C(5)-C(1)-C(1′)	125.5 (5)	C(2)-C(1)-C(1′)	121.2 (5)
C(6)-C(5)-C(5′)	122.6 (5)	C(1)-C(5)-C(5′)	122.6 (5)	C(4)-C(5)-C(5′)	120.1 (5)
C(6)-C(1)-C(5)	58.8 (4)	C(2)-C(1)-C(5)	70.3 (3)	C(1)-C(2)-C(2)	126.0 (5)
C(6)-C(5)-C(1)	61.8 (4)	C(4)-C(5)-C(1)	104.9 (4)	C(3)-C(2)-C(2)	122.0 (5)
C(2)-C(3)-C(3′)	121.9 (5)	C(4)-C(3)-C(3′)	129.3 (6)	C(3)-C(4)-C(4′)	127.6 (6)
C(5)-C(4)-C(4′)	121.2 (5)				

trans gauche conformations (1.48 (10) Å, difference 2.5σ).[10] It is interesting that theoretical calculations of the structure of the parent bicyclo[3.1.0]hexenyl cation not only generally agree with the structure determined here but in particular also show these long bonds between the allyl and cyclopropyl carbons.[11]

As was mentioned above, there is no geometric reason for the lack of conjugation between the cyclopropane and the remainder of the unsaturated system, but rather we conclude that there is an underlying electronic reason for this. We tentatively suggest on the basis of this structure, that the cation undergoes a distortion to minimize the interaction of the cyclopropyl with the allylic portion of **2**. This distortion, or stretching of the C_1,C_2 and C_4,C_5 bonds, is comparable to that encountered in the isoelectronic cyclobutadiene and possibly suggests that **2** can be classified as antihomoaromatic. It should be pointed out, however, that similar anomalous bond distances are also found in the two reported structures of neutral bicyclo[3.1.0]hexenones and several further structures are required before this effect can be fully understood.[12]

Supplementary Material Available: Tables of crystal data, atomic positions, bond lengths and angles, anisotropic temperature factors, and calculated structure factors are available (16 pages). Ordering information is given on any current masthead page.

---

(1) This work was supported by the Natural Science and Engineering Research Council of Canada, McMaster University Science and Engineering Research Board, and Imperial Oil, Ltd.

(2) Childs, R. F. *Acc. Chem. Res.* **1984**, *17*, 347-352.

(3) Vogel, P.; Saunders, M.; Hasty, N. M., Jr.; Benson, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 1551-1552. Childs, R. F.; Winstein, S. *Ibid.* **1974**, *96*, 6409-6417. For a review, see: Barkhash, J. A. *Top. Curr. Chem.* **1984**, *116*, 1-265.

(4) Childs, R. F.; Parrington, B. D.; Zeya, M. *J. Org. Chem.* **1979**, *44*, 4912-4917.

(5) Childs, R. F.; Mahendran, M.; Zweep, S. D.; Shaw, G. S.; Chadda, S. K.; Burke, N. A. D.; George, B. E.; Faggiani, R.; Lock, C. J. L. *Pure Appl. Chem.*, in press.

(6) Childs, R. F.; Faggiani, R.; Lock, C. J. L.; Mahendran, M. *J. Am. Chem. Soc.*, submitted for publication.

(7) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4876-4891.

(8) Arnet, E. M.; Quirk, R. P.; Burke, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 1260-1266.

(9) Childs, R. F.; Faggiani, R.; Lock, C. J. L.; Mahendran, M.; Zweep, S. D. *J. Am. Chem. Soc.*, Preceding paper in this issue.

(10) Allen, F. H. *Acta Crystallogr., Sect. B* **1980**, *B36*, 81-96.

(11) Cremer, D.; Kraka, E.; Slee, T. S.; Bader, R. F. W.; Lau, C. D. H.; Nguyen-Deng, T. T.; MacDougall, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 5069-5075.

(12) Huber, C. O.; Watson, K. J. *J. Chem. Soc. C* **1968**, 2441-2447. Zimmerman, H. E.; Pasterios, R. J. *J. Org. Chem.* **1980**, *45*, 4876-4891.

Quantum Mechanical Prediction of Hydride Locations in Transition-Metal Systems

Carolyn F. Halpin and Michael B. Hall*

Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received September 16, 1985

The task of locating hydrogen atoms in transition-metal compounds has always been a complex and difficult operation. Hence, detailed structural information about the nature of hydrogen-to-metal bonds has been rather limited. Compounds of the series $[\mathrm{HFe(CO)_4M(CO)_5}]^-$ (M = Cr, Mo, W) are no exception.[1] For the W ion, a complete structure determination by X-ray diffraction yielded the atomic positions of all atoms except that of the hydrogen. This complex was originally believed to contain a bridging or semibridging hydride because of the presence of a weak $J_{\mathrm{W-H}}$ coupling of 15.0 Hz.[1] Using the theoretical approach described below, we determined that the hydride ligand in $[\mathrm{HFe(CO)_4Mo(CO)_5}]^-$ is terminally bonded to the iron. The ease of this determination suggests that our method may be competitive with experimental methods for determining H atom positions in metal dimers and clusters.

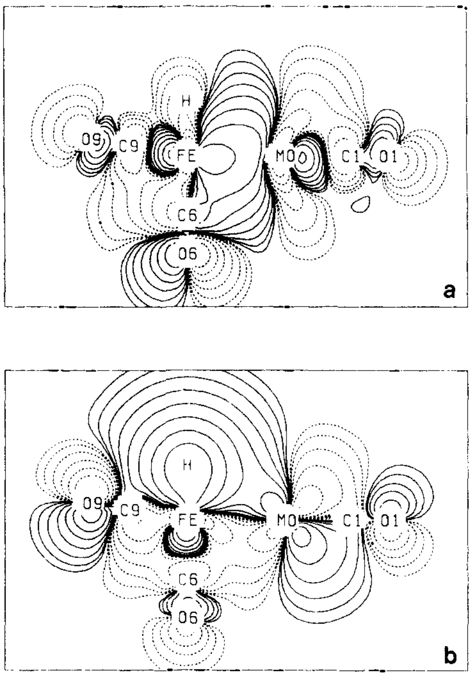


Figure 1. Contour map (a) shows the primary Fe-Mo bonding molecular orbital, which contains more Fe than Mo character and may be viewed as a dative Fe→Mo bond. Contour map (b) shows the primary H-Fe bonding molecular orbital, which contains somewhat more H than Fe character. Both of these delocalized molecular orbitals also contain significant carbonyl character.

As far as accurate bond lengths and angles are concerned, complete characterization of transition-metal hydrides is more complicated than for most other organometallic complexes. Direct location of a hydrogen atom is difficult, since in the most used method of structure determination, X-ray crystallography, the scattering cross section of a hydrogen atom is so small. The problem intensifies as the metal to which the H is bonded becomes heavier or as the number of transition metals in the complex increases.[2-4] From knowledge of ligand dispositions or from the weak electron density peaks in difference Fourier maps, it is possible to indirectly locate hydrogen positions from X-ray data alone.[5,6] Accurate information may be obtained through neutron diffraction, but one needs large well-formed crystals, special facilities, and long collection times.[2,3,6] As an alternative approach, we considered the use of quantum mechanical calculations to locate hydride positions and, therefore, establish a complete structure. An alternative molecular mechanical approach has been suggested by Ciani et al. and Orpen.[7]

Our approach is to use the X-ray structure to fix the positions of all the heavy atoms and to use ab initio molecular orbital calculations to locate the position of the H atom by direct calculation of the total energy for various H atom locations. Since bond distances for both second- and third-row metals are similar, we used the structural data for $[\mathrm{HFe(CO)_4W(CO)_5}]^-$ to fix the positions of the model dianion $[\mathrm{Fe(CO)_4Mo(CO)_5}]^{2-}$. This dianion was then protonated at various positions to map out the potential energy well in which the H is located. The basis functions em-

---

(1) Arndt, L.; Delord, T.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1984**, *106*, 456.

(2) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

(3) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176.

(4) Schultz, A. J.; Stearley, K. L.; Williams, J. M.; Mink, R.; Stucky, G. D. *Inorg. Chem.* **1977**, *16*, 3303.

(5) Churchill, M. R. *Adv. Chem. Ser.* **1978**, *167*, 36.

(6) (a) Petersen, J. L.; Dahl, L. F.; Williams, J. M. *Adv. Chem. Ser.* **1978**, *167*, 11. (b) Ibers, J. A. *Adv. Chem. Ser.* **1978**, *167*, 26.

(7) (a) Ciani, G.; Gusto, D.; Manassero, M.; Albinati, A. *J. Chem. Soc., Dalton Trans.* **1976**, 1943; (b) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

0002-7863/86/1508-1695$01.50/0 © 1986 American Chemical Society