The Mo–Mo distance (2.209 (1) Å) is longer by ca. 0.1 Å than that normally observed in Mo_2 quadruply bonded systems that have been extensively studied by Cotton and co-workers.[15] It seems reasonable to assume a bond order of four that has been lengthened due to the nature of the bridging groups. The short Mo–Mo distance results in an abnormally acute angle subtended at the bridging phosphorus atoms (Mo(1)–P(2)–Mo(1)′ = 53.95 (3)°). This now stands as the most acute M–P–M angle so far reported for a phosphido bridged complex.[16] The strain imposed at P(2) may therefore be partly relieved by a slightly longer than normal Mo$\overset{4}{-}$Mo distance.

The butterfly arrangement of the μ-*t*-Bu_2P groups is also of interest. We have previously suggested that the steric demands of the μ-*t*-Bu_2P unit were largely responsible for planar geometries observed in the M_2P_2 cores of a number of $M_2(\mu\text{-}t\text{-}Bu_2P)_2$ complexes.[2-4] The structure of **1** shows that this is no longer a valid assumption, although the dihedral angle between the Mo(1)–P(2)′–Mo(1)′ and Mo(1)–P(2)–Mo(1)′ planes of 125.9 (5)° is not as severe as those observed in other bis-Ph_2P bridged systems such as $Fe_2(CO)_6(\mu\text{-}Ph_2P)_2$; dihedral angle = 100.0°.[17] The terminal phosphido units are bent back away from the side of the molecule bearing the two bridging groups (Mo(1)–Mo(1)′–P(1)′ = 137.76 (3)°). The coordination geometry about each molybdenum, consisting of two bridging and one terminal phosphorus nuclei, is accurately planar (P(2)–P(2)′–Mo(1)–P(1)). The geometry about each terminal phosphorus is also virtually planar[13] (Mo(1)–P(1)–C(2)–C(1)), and these planes are almost orthogonal to their respective P(1)–P(2)–Mo(1)–P(2)′ planes (85.1°). The planar geometry of the terminal phosphido groups suggests that they act as three-electron donors via additional π donation to Mo as suggested for various dialkylamide derivatives of the transition metals.[18]

The $^{31}P\{^1H\}$ of **1** in toluene-d_8 at −80 °C shows two sharp singlets (1:1) at δ 334.91 and 33.51 (rel 85% H_3PO_4(aq)) assigned to the bridging and terminal phosphorus nuclei, respectively.[19] These signals remain as singlets in the proton-coupled spectrum. The absence of J_{P-P} coupling is presumably a result of different sets of metal orbitals being used for Mo–P(bridge) and Mo–P(terminal) bonding. The structure of **1** with low-coordinate Mo(II) atoms and a large gap on the side of the molecule opposite to the two μ-*t*-Bu_2P groups suggests that it might be unusually reactive. This is consistent with the thermal instability; **1** is unstable in hexane, aromatic (benzene or toluene), or diethyl ether solutions at ambient temperature. The solutions darken rapidly and ^{31}P NMR spectra show the presence of *t*-Bu_2PH (δ 19.41, J_{P-H} = 195.3 Hz in the ^1H-coupled spectrum). No other phosphorus-containing species apart from **1** are detectable in these solutions (^{31}P NMR), and we have been unable to isolate any molybdenum-containing complexes from solutions that have been warmed to room temperature.

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Registry No. 1, 86802-71-3; $Mo_2(O_2CMe)_4$, 14221-06-8; Mo, 7439-98-7.

Supplementary Material Available: Listings of atomic coordinates, thermal parameters, bond lengths and angles, and structure factors (31 pages). Ordering information is given on any current masthead page.

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(15) See: Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; p 89.

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Electron Correlation and Basis Set Effects on the Relative Stabilities of Classical and Nonclassical Structures of the 2-Norbornyl Cation

M. Yoshimine, A. D. McLean, and B. Liu*

IBM Research Laboratory
San Jose, California 95193

D. J. DeFrees

Molecular Research Institute
Palo Alto, California 94304

J. S. Binkley

Sandia National Laboratory
Livermore, California 94550

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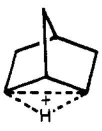
Our ab initio SCF and CI calculations indicate that the potential surface of the 2-norbornyl cation has a minimum corresponding to a nonclassical structure (**1**) and no minimum corresponding to a classical structure (**2**). It follows that, in the gas phase, the 2-norbornyl cation has a symmetrical, carbon-bridged structure, and there is no classical ion. The SCF calculations, using extended basis sets, show that the classical and H-bridged, edge-protonated nortricyclene (**3**) structures found by a previous 4-21G SCF calculation[1] are respectively an artifact of the limited basis set and a saddle point on the potential surface.


(1)


(2)


(3)

The single and double CI calculations, with quadruple-excitation contributions estimated by Davidson's formula,[2] performed at the three stationary points on the 4-21G SCF potential surface,[1] show that electron correlation significantly favors the nonclassical structures over the classical structure. This work was motivated by the long-standing nonclassical ion controversy[3] and the recent low-temperature, solid-state, ^{13}C NMR study of the 2-norbornyl cation by Yannoni, Macho, and Myhre.[4] Previous theoretical studies of the 2-norbornyl cation have been inconclusive due to inadequate basis sets and/or limited treatment of electron correlation effects. A review of recent theoretical work on the 2-norbornyl cation can be found in ref 1.

We have performed SCF structure optimization and analytic force constant calculations using the GAUSSIAN82 program[5] and

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Table I. SCF Total Energies in Hartrees for the C-Bridged 2-Norbornyl Cation and Relative Energies in Hartrees (kcal mol^{-1}) for the Classical and H-Bridged Structures[a]

basis	total energy C bridged	relative energy	
		classical	H bridged
DZ	−271.107 15	−0.001 57 (−1.0)	+0.026 74 (+16.8)
DZD	−271.231 80	−0.000 19 (−0.1)	+0.018 76 (+11.8)
DZDP	−271.252 80	−0.000 09 (−0.05)	+0.016 12 (+10.1)
TZ	−271.130 59	−0.000 78 (−0.5)	+0.023 90 (+15.0)
TZD	−271.251 26	+0.000 59 (+0.4)	+0.019 80 (+12.4)
TZDD	−271.256 58	+0.000 69 (+0.4)	
TZDP	−271.273 97	+0.000 78 (+0.5)	+0.018 06 (+11.3)

[a] All calculations were performed at the optimized 4-21G SCF geometries.

a 4-31G basis.[6] The 4-31G structures are in good agreement with the 4-21G structures. Both bases give partially bridged classical structures; the difference between the 4-31G classical and C-bridged structures is even less than was observed for the corresponding 4-21G structures.[1] On the 4-31G potential surface, the classical structure is a minimum, while the C- and H-bridged structures are saddle points with single imaginary frequencies of 136 and 798 cm^{-1}, respectively. Structure optimization using 6-31G* SCF wave functions yielded bridged structures in good agreement with the corresponding 4-31G structures. However, 6-31G* calculations starting from the 4-31G classical structure converged to the C-bridged structure. An extensive search using SCF wave functions and STO-3G, 4-31G, and 6-31G* basis sets revealed no additional minima on the potential surface.

Table I documents a systematic approach to the HF-limit energy differences between the 4-21G-optimized 2-norbornyl cation structures. Every improvement of the basis beyond double ζ[7] (DZ) stabilizes the bridged structures relative to the classical. The improvements include: extension to triple ζ (TZ),[8] addition of one set of six Cartesian *d* functions with exponent 0.75 on each carbon (DZD, TZD), addition of two sets of *d* functions with exponents 1.4 and 0.6 on each carbon (TZDD), and addition of one set of *p* functions with exponent 0.9 on each hydrogen (DZDP, TZDP). For the TZD, TZDD, and TZDP bases, the C-bridged structure is more stable than the classical. Therefore, in the HF limit, the 4-21G C-bridged structure should be lower in energy than the 4-21G classical structure. Additional TZD and TZDD SCF calculations along an approximate reaction path between the 4-21G classical and C-bridged structures indicated a potential curve with a single minimum at the C-bridged structure. Thus, the true HF potential surface most probably has a C-bridged minimum near the corresponding 4-21G structure and no other stationary points near the 4-21G classical structure. The 4-21G classical ion then must be an artifact of the limited basis set. The results described in this and the preceding paragraphs strongly suggest that the true HF potential surface has no minimum corresponding to a classical structure.

Our CI calculations used a DZD′ basis, obtained from DZD by deleting (1) the 3*s* component of each set of Cartesian *d* functions and (2) all *d* functions on carbon 4, the only one unconnected by a σ bond to any one of the three bridged carbons in the C-bridged structure. These calculations used the ALCHEMY II symbolic matrix direct CI program[9] and included all single and double excitations from the SCF configuration, excluding seven core and seven core-complement orbitals, giving 1 432 278, 717 346, and 718 006 configurations for the classical, C-, and H-bridged structures, respectively. The CI energies in Table II show that electron correlation stabilizes the bridged structures relative to the classical. Our best calculations give stabilization energies of 2.1 and 5.4 kcal mol^{-1} for the C- and H-bridged structures, respectively. These values are probably lower bounds to the true stabilization energies, because DZD SDQ calculations generally underestimate correlation effects. Our CI results are in qualitative agreement with the MP2 calculation by Krishnan et al.[10]

Table II. SCF and CI Total Energies in Hartrees for the C-Bridged 2-Norbornyl Cation and Relative Energies in Hartrees (kcal mol^{-1}) for the Classical and H-Bridged Structures[a]

calculation	total energy C bridged	relative energy	
		classical	H bridged
SCF(DZ)	−271.107 15	−0.001 57 (−1.0)	+0.026 74 (+16.8)
SDCI(DZ)	−271.638 56	−0.000 16 (−0.1)	+0.026 12 (+16.4)
SDQ(DZ)	−271.727 26	+0.000 86 (+0.5)	+0.026 40 (+16.6)
SCF(DZD′)	−271.212 27	−0.000 20 (−0.1)	+0.018 76 (+11.8)
SDCI(DZD′)	−271.927 65	+0.001 34 (+0.8)	+0.015 17 (+9.5)
SDQ(DZD′)	−272.055 97	+0.003 26 (+2.0)	+0.013 51 (+8.5)

[a] All calculations were performed at the optimized 4-21G SCF geometries.

Some conclusions about the shape of the true potential surface of the 2-norbornyl cation follow from our results. Since correlation favors a C-bridged structure that is a minimum on the HF surface, it should also be a minimum on the true surface. Our failure to find a minimum near the 4-21G classical structure on the 6-31G* and TZD SCF surfaces, our failure to find additional classical SCF structures, and the relative magnitudes of the correlation energy contributions all point to a true potential surface with no minimum-energy structure corresponding to the classical ion.

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Registry No. 2-Norbornyl cation, 24321-81-1.

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Stabilization of an α-Diazo Thioketone (a New Class of Compound) by a Unique Linear Triiron Cluster[1a]

Keith H. Pannell,*[1b] Armin J. Mayr,[1b] and
Don VanDerveer[1c]

Departments of Chemistry
The University of Texas at El Paso
El Paso, Texas 79968
The Georgia Institute of Technology
Atlanta, Georgia 30332

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Whereas α-diazo ketones are well-established compounds with some synthetic utility,[2] the corresponding α-diazo thio(seleno)ketones are unknown. Isomeric 1,2,3-thia(selena)diazoles do exist and also have a synthetic utility as intermediates in the synthesis of acetylenes and heterocyclic compounds.[3,4] Oxadiazoles are not known, while 1,2,3-triazoles and their isomeric α-diazo imines exist in thermal equilibrium.[5,6]

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