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Methane Dication: Planar but Not Square

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The doubly charged ion of methane (CH_4^{2+}) is of fundamental importance among gas-phase dications[1] and has been the subject of many experimental[2] and theoretical[2d,3] studies. The highlight of the theoretical studies has been the demonstration that the methane dication is the simplest species containing a planar, tetracoordinate carbon atom. The best theoretical calculations to date[3c,d] have indicated that CH_4^{2+} has an anti-van't Hoff square-planar (D_{4h}) geometry, in contrast to the tetrahedral (T_d) structure of neutral methane, and *this conclusion has been widely accepted.*

We show here, through calculations of the geometry at much higher levels of theory than those previously employed, that *the methane dication is planar but distinctly not square.* The square-planar (D_{4h}) geometry of CH_4^{2+} does not in fact correspond to a minimum on the potential energy surface at the higher levels of theory. The preferred structure of CH_4^{2+} is found to be planar with C_{2v} (rather than D_{4h}) symmetry and is characterized by two long and two short C–H bonds and a narrow HCH bond angle between the two longer C–H bonds. It thus resembles a complex between the methylene dication (CH_2^{2+}) and a hydrogen molecule.

Our initial ab initio calculations[4,5] involved geometry optimizations of C_{2v} (**1**) and D_{4h} (**2**) structures of CH_4^{2+} (see Figure 1) with three different basis sets, namely 6-31G*, 6-31G**, and 6-311G**, and with electron correlation incorporated via Møller–Plesset perturbation theory terminated at second (MP2)-, third (MP3)-, or fourth (MP4)-order,[8] via configuration interaction calculations with single and double substitutions (CISD),[8] or via full-valence CASSCF theory.[9] A selection of optimized geometries is shown in Table I and corresponding total and relative energies in Table II.[10]

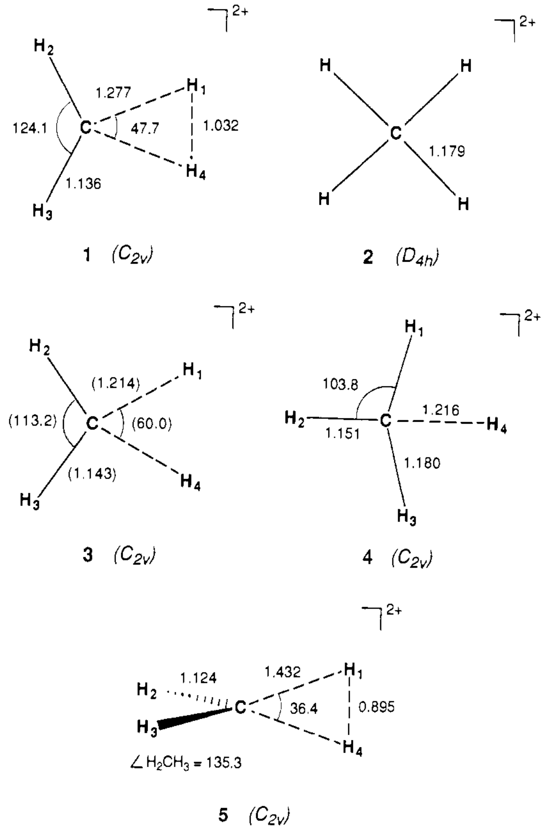

Figure 1. Optimized structures (MP3/6-311G** values, with MP2/6-31G* values in parentheses) for methane dication.

With the (smallest) 6-31G* basis set, both C_{2v} (**1**) and D_{4h} (**2**) structures of methane dication are found to be stable minima (confirmed by frequency calculations at both Hartree–Fock and MP2 levels) on the potential energy surface. The C_{2v} structure (**1**) resembles a complex between the CH_2^{2+} dication and a hydrogen molecule and thus is strikingly different from the D_{4h} form (**2**), but the energies of **1** and **2** are very similar (Table II). At the MP2/6-31G* level, we have located a transition structure **3** (Figure 1) connecting **1** and **2**, but it lies just 1 kJ mol^{-1} above **1**.

Calculations with the inclusion of p polarization functions on hydrogen (6-31G* → 6-31G**) favor strongly the C_{2v} structure (Table II). Although the D_{4h} geometry (**2**) is a true minimum at the HF/6-31G** level, at the MP2 level it corresponds to a second-order saddle point (as shown by a degenerate pair of imaginary frequencies). Rearrangement of **2** (at MP2/6-31G**) along the normal coordinates representing these frequencies leads without a barrier to **1**.

The results for the triple-ζ valence 6-311G** basis set confirm the strong preference for the C_{2v} structure **1** over the D_{4h} form **2**. With this basis set, the D_{4h} structure **2** is no longer a local minimum on the CH_4^{2+} potential energy surface: it represents a second-order saddle point at both Hartree–Fock and MP2 levels. The preferred planar C_{2v} structure **1** is characterized by the following harmonic vibrational frequencies (MP2/6-311G**, scaled[11] by 0.93): 906 (a_1), 942 (b_2), 1022 (a_2), 1105 (b_1), 1426 (a_1), 1608 (b_2), 2163 (a_1), 2570 (a_1), and 2671 (b_2) cm^{-1}. At our best level of optimization (MP3/6-311G**), **1** has a bond angle H_1CH_4 of 47.7° and bond lengths C–H_1 and C–H_2 of 1.277 and 1.136 Å, respectively. The $H_1 \cdots H_4$ distance is 1.032 Å (Figure 1).

Results at still higher levels of theory (Table II) indicate that there is little change in the relative energy in going from the 6-311G** to the 6-311G(2d,2p) basis, while inclusion of diffuse functions and f polarization functions reduces the relative energy by about 3 kJ mol^{-1}. It is evident that all calculations using basis

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Table I. Optimized Geometries for the Planar C_{2v} (**1**) and D_{4h} (**2**) Structures of CH_4^{2+}

	C_{2v} (1)					D_{4h} (2)
	r(C–H$_1$)	r(C–H$_2$)	r(H$_1$–H$_4$)[a]	∠H$_1$CH$_4$	∠H$_2$CH$_3$	r(C–H)
HF/6-31G*	1.238	1.119	1.000	47.7	122.2	1.167
MP2/6-31G*	1.232	1.136	1.085	52.3	118.8	1.176
HF/6-31G**	1.256	1.119	0.988	46.3	123.8	1.166
MP2/6-31G**	1.250	1.127	1.022	48.3	122.7	1.170
HF/6-311G**	1.275	1.120	0.995	45.9	124.8	1.169
MP2/6-311G**	1.268	1.134	1.046	48.7	123.2	1.177
MP3/6-311G**	1.277	1.136	1.032	47.7	124.1	1.179
CISD/6-311G**	1.280	1.134	1.022	47.0	124.5	1.178
CASSCF/6-311G**	1.304	1.143	1.002	45.2	126.2	1.193

[a] Nonindependent parameter, included for completeness.

Table II. Calculated Total Energies (hartrees) and Relative Energies (kJ mol^{-1}) for the Planar C_{2v} (**1**) and D_{4h} (**2**) Structures of CH_4^{2+}[a]

	total energies[b]		relative energies	
	C_{2v} (1)	D_{4h} (2)	C_{2v} (1)	D_{4h} (2)
HF/6-31G*	-39.04744 (0)	-39.04694 (0)	0	1.3
MP2/6-31G*	-39.15268 (0)	-39.15491 (0)	0	-5.9
MP3/6-31G*	-39.16597	-39.16805	0	-5.5
MP4/6-31G*	-39.17050	-39.17245	0	-5.1
CISD/6-31G*	-39.16657	-39.16849	0	-5.0
CASSCF/6-31G*	-39.12776	-39.12729	0	1.2
HF/6-31G**	-39.06549 (0)	-39.05821 (0)	0	19.1
MP2/6-31G**	-39.18474 (0)	-39.17961 (2)	0	13.5
HF/6-311G**	-39.07680 (0)	-39.06668 (2)	0	26.6
MP2/6-311G**	-39.21196 (0)	-39.20642 (2)	0	14.5
MP3/6-311G**	-39.21293	-39.20668	0	16.4
CISD/6-311G**	-39.21285	-39.20590	0	18.2
CASSCF/6-311G**	-39.15928	-39.14844	0	28.5
MP4/6-311G(2d,2p)[c]	-39.22505	-39.21882	0	16.4
ST4CCD/6-311G(2d,2p)[c]	-39.22646	-39.22012	0	16.6
HF/6-311+G(2df,2p)[c]	-39.07944	-39.06941	0	26.3
MP2/6-311+G(2df,2p)[c]	-39.21046	-39.20589	0	12.0
MP3/6-311+G(2df,2p)[c]	-39.22948	-39.22471	0	12.5
MP4/6-311+G(2df,2p)[c]	-39.23504	-39.23007	0	13.0
CCD/6-311+G(2df,2p)[c]	-39.23244	-39.22703	0	14.2
ST4CCD/6-311+G(2df,2p)[c]	-39.23640	-39.23129	0	13.4

[a] Geometries fully optimized at the level specified, unless otherwise noted. [b] Number of imaginary frequencies in parentheses. [c] MP3/6-311G** optimized structures.

sets larger than 6-31G* clearly favor the C_{2v} structure **1** over the D_{4h} structure **2**. At our best level of theory, which involves large basis set coupled-cluster calculations at the ST4CCD level[12] (ST4CCD/6-311 + G(2df,2p)), the C_{2v} structure **1** is more stable than the D_{4h} structure **2** by 13 kJ mol^{-1}. Zero-point vibrational correction leads to a final prediction of 4 kJ mol^{-1}.[13]

As noted earlier, the C_{2v} structure **1** can be regarded as a complex of the methylene dication and a hydrogen molecule. The calculated stabilization energy associated with this three-center two-electron (3c-2e) donor–acceptor interaction[14,15] is 381 kJ mol^{-1}.[16] A similar donor–acceptor complex has been reported[17] for the second-row analogue SiH_4^{2+}. We note also that 3c-2e stabilization is a common structural feature in other carbodications: for example, CH_6^{2+},[18] $C_2H_6^{2+}$,[19] $C_2H_8^{2+}$,[19] and $C_3H_8^{2+}$.[20,21]

We have located a transition structure **4** for hydrogen scrambling in **1**, but its energy is only 4 kJ mol^{-1} above **1**. Hydrogen scrambling in **1** should, therefore, be very rapid, and the experimental identification of nonequivalent hydrogens in the planar C_{2v} structure will not be straightforward.

The perpendicular C_{2v} structure **5** lies 54 kJ mol^{-1} higher than **1** and corresponds to a rotational transition structure. It represents a weaker complex than the planar form **1**, as reflected by the longer C–H$_1$ bond (1.432 Å) and shorter H$_1$–H$_4$ distance (0.895 Å). The preference for the planar structure **1** can be rationalized in terms of the back-donation from the pseudo-π orbital of the CH_2^{2+} group in **1** to the σ^* orbital of H_2.

In conclusion, we have confirmed that the methane dication prefers a planar anti-van't Hoff geometry. We have shown, however, that it has C_{2v} symmetry rather than the previously accepted square-planar D_{4h} structure.

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