A Density Functional Study of the Rotational Barrier of Tricarbonyl(η^4-norbornadiene)iron. Effect of the Torsional Angle on the Carbonyl Stretching Spectra

Michael Bühl and Walter Thiel*

Organisch-Chemisches Institut, Universität Zürich,
Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

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Introduction

The time scale of infrared spectroscopy is so fast that dynamic processes usually escape detection. One notable exception is the variable-temperature IR spectrum of tricarbonyl(η^4-norbornadiene)iron (**1**):[1−4] At low temperature, three ν(CO) stretching signals are found, as expected for a static C_s symmetrical structure. As the temperature increases, two of these bands collapse or coalesce into a single one, reminiscent of the well-known phenomenon in dynamic NMR spectroscopy. Assuming a very rapid site exchange which renders the three CO groups vibrationally equivalent (affording pseudo-C_{3v} symmetry), a barrier of ca. 1.5 kcal/mol has been deduced by line-shape analysis.[2,3]

A possible mechanism for this site exchange is a turnstile rotation of the Fe(CO)$_3$ unit relative to the norbornadiene moiety, with a very rapid "hopping" from one well to the other on the potential energy surface (PES).[1,4] Alternatively, it has been suggested that the broadening and apparent coalescence of the two IR bands could be explained by thermal motions of the carbonyls in one potential well:[5] The amplitude of torsion of the Fe(CO)$_3$ unit within this well would increase with the temperature which would account for the observed effects provided that the CO stretching frequencies would change steeply over the range of motion in the single well. It has therefore been suggested to perform "ab initio calculations of the vibrations of **1** as a function of torsional angle".[5]

In recent years, the modern tools of density functional theory (DFT) have evolved to a point[6] which now allows the theoretical investigation of this problem. In particular, it has been shown that the vibrational spectra of transition metal carbonyls and carbonyl hydrides are well reproduced at gradient-corrected DFT levels,[7,8] with an accuracy of typically 10−40 cm^{-1}. Moreover, the deviations from experiment are quite systematic for various types of vibrations, e.g. for CO stretching frequencies, so that relative trends, such as those suggested for **1**, should be predicted reliably. We now present theoretical results pertinent to the dynamics of **1**. Special attention is called to the dependence of the computed ν(CO) stretching frequencies on the torsional angle. Further calibration of the methods employed is provided by the results for a closely related system, Fe(CO)$_3$(η^4-butadiene) (**2**).

Computational Details

Calculations were carried out at the BP86/AE1 level of DFT, i.e. with the gradient corrections for exchange and correlation from Becke[9] and Perdew,[10] respectively, Wachters' (14s11p6d)/[8s7p4d] all-electron basis for Fe,[11] augmented with two additional 4p functions[11] and a diffuse d function,[12] and standard 6-31G* basis[13] on the ligands. This is the same level as used in the studies of transition metal carbonyls[7] and carbonyl hydrides[8] (in the latter, polarization functions have also been employed for the hydrogens attached to the metal).

Geometries have been fully optimized in C_s symmetry, and frequencies have been computed from analytical second derivatives. A rotamer of **1** has been partially optimized in C_1 symmetry (see below). Unless noted otherwise, energies are reported at the BP86/AE1 + ZPE level, i.e. including the BP86/AE1 zero point correction. All computations employed the Gaussian 94 package,[14] and spherical d functions were used throughout.

Results and Discussion

As a first test of the theoretical methods employed, we have computed the IR frequencies and the rotational barrier of Fe(CO)$_3$(η^4-butadiene) (**2**). Unlike in the case of **1**, there are no unusual features in the variable-temperature IR spectrum of **2**, and the pattern of three ν(CO) bands expected for a static C_s structure is found at room temperature.[3] On the NMR time scale, however, **2** is fluxional:[15,16] The two carbonyl δ(^{13}C) signals corresponding to the static C_s structure are only observed below ca. −60 °C where they coalesce into a single resoncance. An enthalpy of activation of 9.1(±0.5) kcal/mol has been deduced[16] for the scrambling process.

The BP86/AE1 optimized geometries of **2** and of the transition state for rotation, **2(TS),** are displayed in Figure 1. In **2(TS)**, the Fe(CO)$_3$ moiety is rotated by approximately 60° with respect to **2**. C_s-symmetric **2(TS)** is a true transition state with one imaginary frequency (78i cm^{-1}) rather than an intermediate. The computed barrier for rotation, 9.4 kcal/mol, is in excellent accord with the experimental estimates. Likewise, the BP86/AE1 ν(CO) stretching frequencies of **2** agree nicely with the experimental data (see Figure 1). In particular, the separation $\Delta\nu$ of the two lower modes (a″ and a′), which would become degenerate upon rapid exchange, is well reproduced, calcd 10 vs exptl 11 cm^{-1}. It thus appears that the theoretical level employed is sufficient for this type of compounds and that the following results for the title compound **1** should be reliable.

The optimized geometries of **1** and the transition structure **1(TS)** are shown in Figure 2, together with the computed ν(CO) stretching frequencies. Going from **1** to **1(TS)** requires a rotation of the Fe(CO)$_3$ unit of only ca. 30°, compared with ca. 60° in the case of **2**. The rotation should therefore be more facile in **1** than in **2**. The calculated rotational barrier for **1** is

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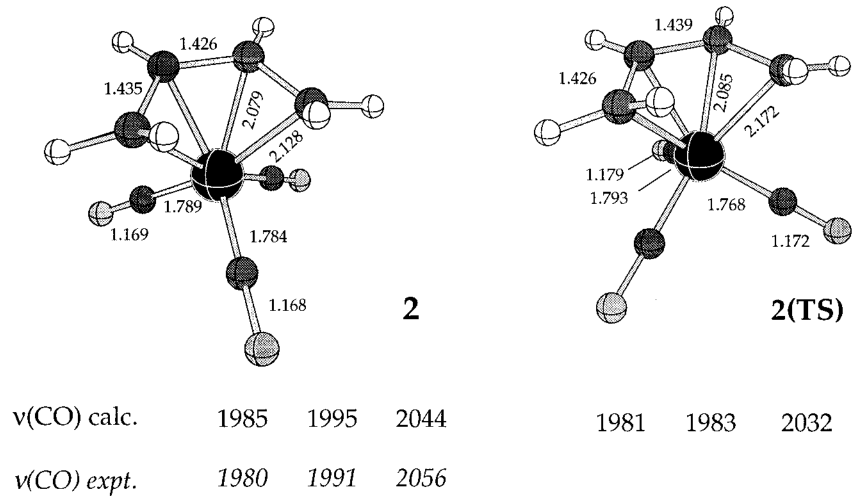

Figure 1. BP86/AE1 optimized geometries of $Fe(CO)_3(\eta^4$-butadiene), **2**, and the transition state for $Fe(CO)_3$ rotation, **2(TS)**. The calculated ν(CO) stretching frequencies are included, together with the experimental numbers from ref 3 (isooctane, 20 °C).

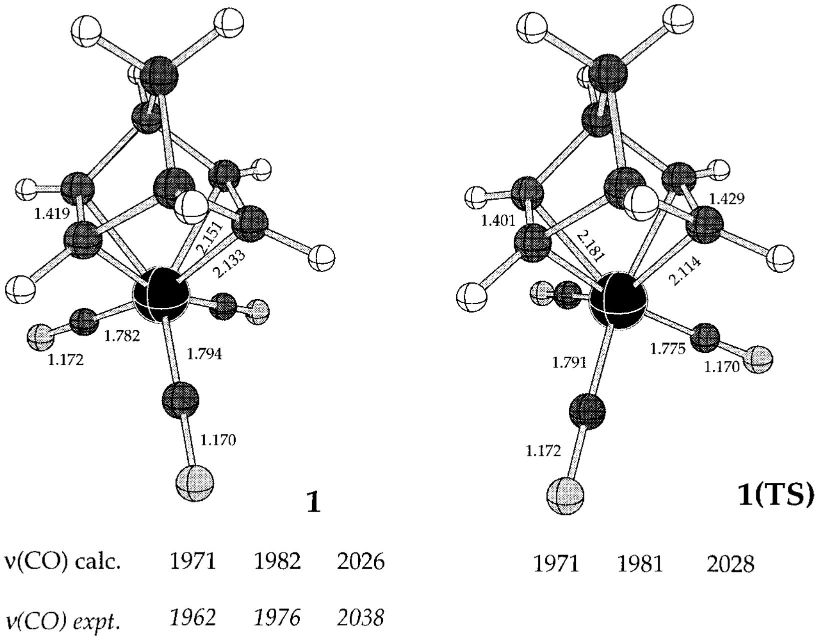

Figure 2. BP86/AE1 optimized geometries of $Fe(CO)_3(\eta^4$-norbornadiene), **1**, and the transition state for $Fe(CO)_3$ rotation, **1(TS)**. The calculated ν(CO) stretching frequencies are included, together with the experimental low-temperature data from ref 1 (liquid Kr/Xe, −146 °C).

indeed only 0.5 kcal/mol (0.6 kcal/mol without zero point correction), i.e. somewhat smaller than the experimental estimates[2,3] around ca. 1.5 kcal/mol. Compared to **2**, the PES for rotation of the $Fe(CO)_3$ group is extremely flat, which is also reflected in the very small values of the torsional frequency for **1**, 34 cm^{-1}, and the corresponding imaginary frequency for **1(TS)**, 35*i* cm^{-1}. Consequently, very rapid rotation and, thus, CO site exchange might be expected for all but very low temperatures.

Computed and experimental ν(CO) stretching frequencies of **1** are in good accord (Figure 2). As in the case of **2**, the difference Δν between the two lowest CO stretching modes is well reproduced theoretically (calcd 11, exptl 14 cm^{-1}). Interestingly, the corresponding frequencies in **1(TS)** are virtually identical to those of **1**, affording practically the same predicted Δν (10 cm^{-1}; cf. Figure 2). In contrast, for the butadiene derivative **2** these two modes are predicted to shift closer together in the transition state, with a separation of only 2 cm^{-1} in **2(TS)**; cf. Figure 1.

Apparently, Δν of **1** is quite insensitive to the relative conformation of the $Fe(CO)_3$ and the norbornadiene moieties. In addition to the stationary points **1** and **1(TS)** in Figure 2, this was also tested for an intermediate form with the $Fe(CO)_3$ group rotated by 15°. For this purpose, the torsional angle beetween one Fe−CO and one methylene HC−H bond[17] was fixed to this value, and all other geometrical parameters were optimized without any symmetry constraints. At the BP86/AE1 level, such a partially optimized structure is 0.3 kcal/mol above the minimum. The corresponding CO stretching frequencies (1971, 1982, and 2027 cm^{-1}) are computed in between and essentially identical to those of **1** and **1(TS)**. Therefore, these results provide no evidence for a change of the CO stretching modes upon intrawell torsional motion.

Conclusion

The DFT results presented indicate that the CO site exchange in $Fe(CO)_3(\eta^4$-norbornadiene) (**1**) and $Fe(CO)_3(\eta^4$-butadiene)

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[17] Viewed along a line passing through the methylene carbon and the iron atom, one Fe−CO and one HC−H bond are perfectly eclipsed in **1(TS)**, while the smallest corresponding dihedral angle is ca. 30° in **1**.

(**2**) proceeds via a turnstile rotation of the $Fe(CO)_3$ and diene moieties. The rotational barrier for the former is 1 order of magnitude smaller than for the latter at the BP86/AE1 + ZPE level, consistent with the experimental data. From the very small barrier for **1**, between 0.5 (computed) and ca. 1.5 kcal/mol (experiment), a very rapid rotation and CO site exchange would be expected, thereby giving rise to the coalescence of two ν(CO) bands observed in the variable-temperature IR spectra. An alternative explanation for this apparent coalescence, which involves thermal motions of the carbonyls in one potential well and which requires changes in the CO stretching frequencies with this torsional motion, is not supported: The computed ν(CO) frequencies are virtually independent of the torsion, i.e. the relative conformation, of the $Fe(CO)_3$ and norbornadiene units.

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