Can carbon monoxide polymerize? A theoretical investigation of polyketone

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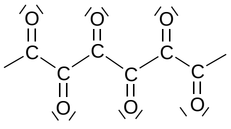
State of the art *ab initio* calculations on $R(CO)_nR$ (R = H, Me; n = 1–11) indicate that the hypothetical polymer of carbon monoxide, poly-CO, would be energetically less stable than the molecular form only by a few kcal mol^{-1}, making it a plausible stable allotropic form of CO.

Predictive quantum chemistry offers the opportunity to design new polymers with potentially interesting physical or structural properties. One can design these new materials by linking building blocks which sometimes can exist alternatively as stable monomers, dimers or even larger finite aggregates.[1–3] Our contribution in this field concerns the investigation of a hypothetical polymer of carbon monoxide by means of *ab initio* and density functional calculations. This polymer **1**, named poly-CO throughout this paper, has the unusual property of having a repeat unit that is isoelectronic, albeit not isodesmic, to molecular CO: the [C=O] repeat units are linked together through C(sp^2)–C(sp^2) single bonds. Standard bond energy calculations[4] indicate that CO polymerization should be roughly thermoneutral, suggesting that poly-CO should be thermodynamically stable. Moreover, vicinal oligoketones, $R(CO)_nR$ (n < 6), have been shown to exist,[5] as well as one-dimensional $(BC)^{3-}$ chains, isoelectronic to poly-CO, which are encountered in several MBC (M = rare earth metal) solid state phases.[6] Previous semi-empirical calculations by some of us[7] and by Hoffmann[8] on poly-CO suggest that it should have an helical conformation.



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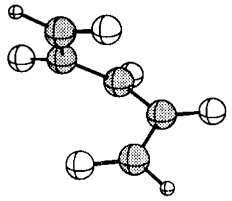
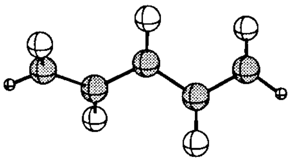
We have evaluated the poly-CO total energy per repeat unit from calculations on a series of linear $R(CO)_nR$ (R = H, Me) oligomers by using the finite difference method.[9] Assuming that, for a given n value, E_n is the total energy of the most stable conformer of $R(CO)_nR$, the difference function $\Delta E_n = E_{n+1} - E_n$ is expected to tend to the poly-CO energy per CO unit when n becomes large enough. We have performed *ab initio* and DFT calculations§ on $R(CO)_nR$ (R = H, Me) oligoketones, up to n = 11.¶ The corresponding $\Delta E_n - E(CO)$ energy values are shown in Fig. 1.

The potential energy surface was fully explored up to n = 5 for R = H. In this case, for example, seven conformational isomers were identified, all differing from the relative rotational orientation of their CO groups. All these conformers lie in an energy range of *ca.* 8 kcal mol^{-1}, the four lowest in energy differing by less than 3 kcal mol^{-1}. It is worth noting that for $R(CO)_5R$ (R = H, Me) the lowest energy corresponds to the helical form, **2a**, a conformation experimentally observed for $Ph(CO)_nBu^t$.[5d,e] The second lowest in energy corresponds to the all-*trans* conformation **2b** lying above **2a** by less than 1.5 kcal mol^{-1}‖ From these results it is clear that the potential energy surface associated with the conformational fluxionality of oligoketones is particularly soft.** For larger oligomers, the number of conformations becomes too large to allow a full structural investigation, and we restricted our research to isomers having the C_2 symmetry. It turns out that for n > 2, all the optimized conformers are non-planar and typical C–C and C=O bond lengths are computed. The carbon atoms always maintain their expected (locally planar) sp^2 hybridization. Therefore, the conformation of the oligoketones can simply be described by the series of the dihedral angles (α) between adjacent CO units, which are reported in supplementary material.‖



2a, TCCT



2b, TTTT

From Fig. 1, one may see that the ΔE_n variations computed at the HF and B3LYP geometries behave similarly, showing that optimized HF geometries can be used, allowing the study of longer $H(CO)_nH$ chains up to n = 11. Furthermore, the calculations performed with R = Me for smaller n values provide evidence that no special end effect is present in the calculations with R = H. It is clear that for n = 9 the parity oscillations due to the small-size effect are damped, as well as the asymptotic value of ΔE_n is nearly reached. When ZPVE corrections are included,§ poly-CO is computed to be less stable

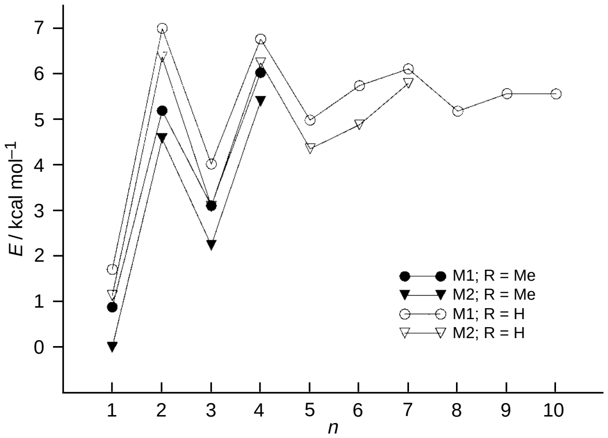


Fig. 1 Plots of $E[R(CO)_nR] - E[R(CO)_nR] - E[CO]$ (R = H, Me) with respect to n. Calculations are made at the B3LYP/6-311 + G**//HF/6-31G** (M1) and B3LYP/6-311 + G**//B3LYP/6-31G** (M2) levels, including ZPVE corrections. Filled and empty symbols are for (Me)-$(CO)_n$(Me) and $H(CO)_nH$ oligomers, respectively.

than free CO monomer by only 5.5 kcal mol^{-1}. However, ZPVE terms are obtained assuming isolated molecules, while the hypothetical polymer is expected to exist as a solid in which the vibrational energy could be different. Discarding ZPVE corrections leads to an even smaller energy difference (3.5 kcal mol^{-1}). Dipole–dipole and van der Waals interactions, present in the solid-state phase of the polymer, are not taken into account in this study. They may reduce this energy difference or even perhaps change its sign. Moreover, as the potential energy surfaces of the studied oligoketones is particularly flat, the conformation of poly-CO in the hypothetical condensed phase (as under high pressure) may be different from the calculated gas phase helical conformation.[7] In any case, these calculations strongly suggest that poly-CO is a stable allotropic variation of carbon monoxide. The crucial point for its synthesis would be to overcome kinetic problems.

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Footnotes and References

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§ Geometry optimisations were carried out with the use of the GAUSSIAN 94 package[10] at the HF, MP2 and B3LYP levels, using the 6-31G** basis set. Harmonic vibrational frequencies and zero-point vibrational energies (ZPVE) were computed at HF level for all systems and in some cases, at the MP2 and B3LYP levels. Single point B3LYP calculations using the larger 6-311 + G** basis set were also performed on the optimised geometries. Since the three levels of calculations lead to similar qualitative conclusions, only single-point B3LYP/6-311 + G** energies on the optimised geometries [HF (M1) and B3LYP/6-31G** (M2)] are discussed here.

¶ The stability of finite oligomers, such as C_2O_2 or cyclic C_nO_n molecules, has been discussed.[5a,11] Our preliminary calculations on these cyclic species indicate that they are significantly less stable than free CO, at least for $n < 9$ (to be published).

‖ Tables which summarize the main energetic and conformational data of the most stable $R(CO)_nR$ conformers can be requested from the authors.

** A critical factor related to the energy of these species in their planarity or non-planarity. Conjugation, *i.e.* π–π^* mixing, tends to favor planarity. On the other hand, a second-order Peierls distortion away from planarity, associated to σ_n–π mixing is expected for poly-CO. O··O lone pair repulsions also disfavour planar conformations. Finally, non-bonding interactions involving the terminal R groups can also play some role in the conformational choice, by forming weak intramolecular hydrogen bonds.[5,7,12]

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