

Significant evidence of C $\cdots$ O and C $\cdots$ C long-range contacts in several heterodimeric complexes of CO with CH<sub>3</sub>-X, should one refer to them as carbon- and dicarbon-bonds!

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## Supplementary information

### Computational Details.

The structures of the monomers and the binary complexes are energy-minimized using Density Functional Theory Method (DFT) at PBE1PBE (in short, PBE0)<sup>1</sup> in conjunction with a valence quality triple- $\zeta$  Gaussian type basis set, 6-311++G(d,p), augmented with 1 set of each of the d and p functions. Uses of these computational methods have resulted the monomer structural and dipole moment properties comparable with their available experimental data,<sup>2</sup> thereby these are probably adequate to model the complexes. Hessian calculations are performed analytically to calculate the eigenvalues, and normal mode frequencies of the monomers and complexes. The positive eigenvalues are found for all the cases (except for structure Figure 4g, which is a second order saddle point), this confirms the structures reported are a local minima on their respective PBE0 potential energy surfaces. The recommended ultrafine integration grid, together with tight self-consistent-field criterion, instead of default settings, is employed for the PBE0 method for Hessian calculations.

For reasons discussed elsewhere,<sup>3-5</sup> Natural bond orbital (NBO) analyses are performed with RHF/6-31+G(d,p) to evaluate the second order perturbative energy,  $E^{(2)}$ , caused by the charge transfer hyperconjugative interaction between the electron-donor and -acceptor NBOs. The mathematical form of  $E^{(2)}$  is given by Eq. 1:

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$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_i - \varepsilon_j} \dots\dots\dots(1),$$

where  $\varepsilon_i$  and  $\varepsilon_j$  are the diagonal orbital energies of the donor ( $i$ ) and acceptor ( $j$ ) NBOs, respectively, while  $q_i$  is the donor orbital occupancy, and  $F(i,j)$  is the off-diagonal NBO Fock matrix element. All the calculations are performed using the GAUSSIAN 09 suites of programs.<sup>6</sup> For visualization of the normal mode vibrational frequencies, and generation of the molecular electrostatic potential maps, the GAUSSVIEW 05<sup>7</sup> and MOLEKLE<sup>8</sup> software codes are used.

The Quantum Theory of Atoms in Molecules (QTAIM) calculations are performed using MultiWfn software,<sup>9-10</sup> in combination with the AIMALL software.<sup>11</sup> For this purpose, the wavefunctions are generated on the optimized geometries of the monomers and the complexes using PBE0/6-311++G(d,p) with GAUSSIAN 09. These wavefunction files were served as inputs to the above codes. The various topological properties of charge density obtained (as in Table 2) were evaluated using Proaim basin integration method, fine interatomic surface mesh, and very high basin quadrature. The Noncovalent Interaction Reduced-Density-Gradient (NCI-RDG) plots are performed using NCIPLOT Version 3.0 using medium size grids,<sup>12-13</sup> in combination with VMD,<sup>14</sup> the latter code was used for generating the NCI-RDG isosurfaces.

It is demonstrated in several occasions that an examination of the molecular electrostatic surface potential is very useful for identifying reactive sites (acidic and basic) required for the fundamental understanding of noncovalent interactions.<sup>15-21</sup> This analysis gives the local most positive and most negative areas of electrostatic potential in terms of exact positions and magnitudes, and with this knowledge, and using particular substituents, one can even appropriately trigger a particular atomic site in a molecule to make it nucleophilic (electron rich) or electrophilic (electron deficient).<sup>22-24</sup> For instance, it was shown that for a system to hydrogen/halogen/ $\sigma$ -hole bond with a nucleophilic fragment of an interacting partner molecule (or that with the other part of the same molecule) the electrostatic potential on the surface of the hydrogen/halogen/ $\sigma$ -hole containing atom must be a maximum ( $V_{s,max} > 0$ ) and that on the Lewis base must be a minimum ( $V_{s,min} < 0$ ), where 's', 'min' and 'max' refer to the surface, minimum and maximum, respectively.<sup>22,25</sup> The  $V_{s,max}$  of acidic sites, as well as the  $V_{s,min}$  of basic sites, are

also shown to correlate well with the empirical measures of electron-accepting and -donating tendencies, respectively.<sup>25-27</sup> Nevertheless, the concept of electrostatic surface potential is widely applied to systems as diverse as covalently bonded atoms of main group elements of groups 14,<sup>15,17,18,22</sup> 15,<sup>28-29</sup> 16,<sup>30-31</sup> and 17<sup>32-33</sup> to explore various types of nocovalent interactions and their physical properties.

The electrostatic potential,  $V(r)$ , at any point  $r$  due to the nuclei and electrons of a molecule is related to the molecular electron density,  $\rho(r)$ , by Eq. 2.

$$V(r) = V_{nuclei} + V_{electrons} = \sum_A \frac{Z_A}{|r - R_A|} - \int \frac{\rho(r')dr'}{|r - r'|} \dots\dots\dots(2)$$

In this equation,  $Z_A$  is the charge on nucleus  $A$  located at  $R_A$ . Following the recommendations of Bader and others,<sup>34</sup> and using the MultiWfn code,<sup>8</sup> the quantitative values of  $V(r)$  are computed on the molecular surfaces of the  $\sigma$ -hole donor molecules  $\text{CH}_3\text{-X}$ , as well as that on the CO molecule, defined by the 0.001 au (electrons/bohr<sup>3</sup>) contours of electronic densities.

## References

1. C. Adamo, V. Barone, J. Chem. Phys. 1999, 110, 6158.
2. (a) The molecular structural, dipole moment, vibrational, and thermodynamic properties of all the monomers investigated in this study can be found in the NIST Computational Chemistry Comparison and Benchmark Database NIST Standard Reference Database Number 101. Release 16a, August 2013, Editor: R. D. Johnson III. Available via DIALOGUE: <http://cccbdb.nist.gov/>;  
(b) R. D. Nelson Jr., D. R. Lide, A. A. Maryott "Selected Values of electric dipole moments for molecules in the gas phase" NSRDS-NBS10, 1967.
3. F. Weinhold, C. Landis, Valency and Bonding, A Natural Bond Orbital Donor-Acceptor Perspective, Cambridge University Press, New York, 2005
4. I. V. Alabugin, M. Manoharan, S. Peabody, F. Weinhold, J. Am. Chem. Soc. 2003, 125, 5973.
5. F. Weinhold, J. Comput. Chem. 2012, 33, 2363.
6. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M.

- Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
7. GaussView, Version 5, Dennington, R.; Keith, T.; Millam, J. Semichem Inc., Shawnee Mission KS, 2009.
  8. U. Varetto, MOLEKEL 4.3; Swiss National Supercomputing Centre: Lugano (Switzerland)
  9. T. Lu, F. Chen, J. Comp. Chem. 2012, 33, 580.
  10. T. Lu, F. Chen, J. Mol. Graph. Model. 2012, 38, 314.
  11. T. A. Keith, AIMAll (Demo Version 11.03.14), 2011. Available via DIALOG at: <http://im.tkgristmill.com>.
  12. E R. Johnson, S. Keinan, P. Mori-Sanchez, J. Contreras-Garcia, A J. Cohen, and W. Yang, J. Am. Chem. Soc. 2010, 132, 6498.
  13. J. Contreras-Garcia, E. Johnson, S. Keinan, R. Chaudret, J-P Piquemal, D. Beratan, W. Yang, J. Chem. Theor. Comp. 2011, 7, 625.
  14. Humphrey, W., Dalke, A. and Schulten, K., "VMD - Visual Molecular Dynamics", J. Molec. Graphics, 1996, vol. 14, pp. 33-38. The software is available via DIALOGUE: <http://www.ks.uiuc.edu/Research/vmd/>
  15. J. Murray, P. Lane, P. Politzer, J. Mol. Model. 2009, 15, 723.
  16. A. Bundhun, P. Ramasami, J. Murray and P. Politzer, J. Mol. Model. 2012, 1.
  17. P. Politzer and J. S. Murray, Chem. Phys. Chem. 2013, 14, 278.
  18. P. Politzer, J. S. Murray, T. Clark, Phys. Chem. Chem. Phys. 2013,15, 11178.

19. J. S. Murray, P. Politzer, *Croat. Chem. Acta* 2009, 82, 267.
20. J. S. Murray, P. Politzer, *Cryst. Eng. Comm.* 2013, 15, 3145.
21. V. Dimitrova, S. Ilieva, B. Galabov, *J. Mol. Struct. (Theochem)* 2003, 637, 73.
22. A. Bundhun, P. Ramasami, J. S. Murray, P. Politzer, *J. Mol. Model.*, 2013, 2738.
23. P. Politzer, P. Lane, J. S. Murray, *Struct. Chem.* 2013, 24, 1965.
24. K. E. Riley, J. S. Murra, J. Fanfrlík, J. Řezáč, R. J. Solá, M. C. Concha, F. M. Ramos, P. Politzer, *J. Mol. Model.* 2013, 19, 4651.
25. J. S. Murray, P. Politzer, *Overview* 2011, 1, 153.
26. H. Hagelin, J. S. Murray, T. Brinck, M. Berthelot, P. Politzer, *Can. J. Chem.* 1995 73, 483.
27. P. W. Kenny, *J. Chem. Inf. Model.* 2009, 49, 1234.
28. S. Scheiner, *J. Chem. Phys.* 2011, 134, 094315.
29. J. E. Del Bene, I. Alkorta, G. Sanchez-Sanz, J. Elguero, *J. Phys. Chem. A* 2011, 115, 13724.
30. W. Wang, B. Ji and Y. Zhang, *J. Phys. Chem. A*, 2009, 113, 8132–8135.
31. D. Manna, G. Mugesh, *J. Am. Chem. Soc.* 2012, 134, 4269.
32. P. Metrangolo, G. Resnati, *Chem. Eur. J.* 2001, 7, 2511.
33. A. C. Legon, *Phys. Chem. Chem. Phys.* 2010, 12, 7736.
34. R. F. W. Bader, M. T. Carroll, J. R. Cheeseman, C. Chang, *J. Am. Chem. Soc.* 1987, 109, 7968.