Steric Effects in Iron Butterfly Clusters, Fe$_4$(CO)$_{12}$CR, probed by Interactive Molecular Graphics

John M. Newsam and John S. Bradley

Exxon Research and Engineering Company, Route 22 East, Annandale, New Jersey 08801, U.S.A.

Interactive molecular graphics is demonstrated to be a simple yet powerful means of probing semi-quantitatively steric effects in organometallic compounds such as the iron butterfly clusters Fe$_4$(CO)$_{12}$CR in which such effects are found to restrict both the orientation and the nature of the carbido substituent, R.

Recent analyses of the bonding in iron butterfly clusters based on [Fe$_4$(CO)$_{12}$C]$^{2-}$ have provided self-consistent explanations for aspects of their reactivity[1,2] and have given good correlations between their electronic and molecular structures. It has, however, been suggested that the orientation of organic groups bonded to the Fe$_4$(CO)$_{12}$ butterfly, such as the methoxycarbonylmethylidyne group in [Fe$_4$(CO)$_{12}$C–CO$_2$Me]$^-$ (1), might reflect purely steric constraints,[1] implying that nonbonded interactions may play an important role in determining the reaction pathways of such clusters. We have used interactive molecular graphics, a techique that has previously been widely applied to organic and biochemical systems,[3] to probe semi-quantitatively steric restrictions both on the orientation of the organic group, R = CO$_2$Me, in (1) and on the nature of the substituent, R, at the carbido carbon.

Atomic co-ordinates for (1) were taken from the single-crystal X-ray study of Bradley *et al.*[4] The necessary hydrogen atoms were added geometrically. The steric environment of the carbido carbon and the attached ester group was then probed by monitoring the intramolecular van der Waals energy sum computed using the expression and parameters given by Del Re *et al.*[5] as a function of the orientation of this group with respect to the rest of the cluster. Contributions from the iron atoms were not included. Although this description and parameterisation of the nonbonded interactions is simplistic, as the steric effects of interest are dictated mainly by the form of the short-range repulsions it provides a reasonable approximation when considering the relative

energies of different cluster conformations. The energy calculations were made as a function of three parameters, the Fe(1)–C(1)–C(2) angle, ϕ, the Fe(2)–C(1)–C(2) angle, χ, and rotation, θ, of the ester function about the C(1)–C(2) bond (see Figure 1). The remainder of the molecular geometry was fixed at the configuration observed crystallographically.[4] The computations were performed using the CHEMGRAF program package[6] without modification on a VAX 11/750 computer system.

Figure 2 shows the van der Waals energy plotted as a function of one of these parameters, χ. The energy minimum coincides closely with that found in the crystal structure. This minimum is relatively sharp. Even small changes in the Fe(2)–C(1)–C(2) angle, χ, or indeed of the other angles ϕ and θ are accompanied by significant increases in the nonbonded atom–atom repulsions, in agreement with the suggestion of Wijeyesekera *et al.*[1] The range between points of computed energy kT above the minimum spans a range of only some 5° on either side of the energy minimum. Even if we allow considerable margin for the approximate nature of the present description of the short-range interactions, the ester group is seen to be constrained to orientations close to that observed crystallographically.

Interactive molecular graphics also enables us to probe the steric restrictions on C(2) substituents in the environment provided by the Fe$_4$(CO)$_{12}$C unit. Specifically, we have compared the hypothetical clusters, Fe$_4$(CO)$_{12}$CR, R = CH$_2$ [with the CH$_2$ substituent in the same orientation as that of the ester group in (1)] and R = Me. This comparison provides a simple yet direct way of monitoring the differing steric requirements of sp^2 and sp^3 hybridisation at C(2). Even after
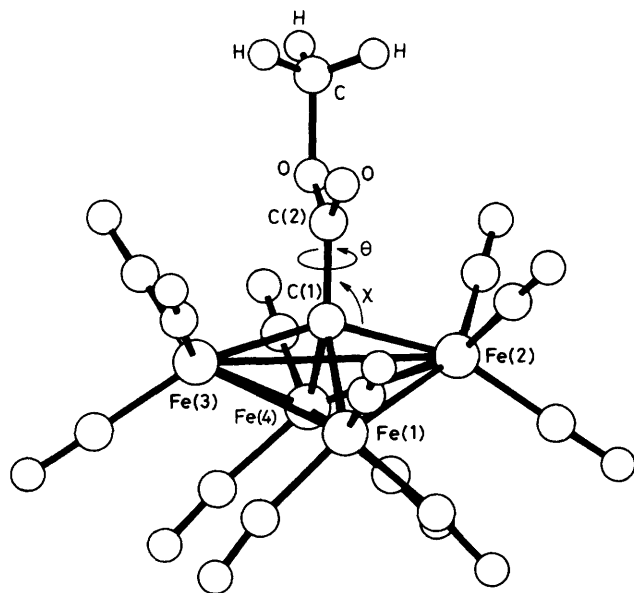

Figure 1. The [Fe$_4$(CO)$_{12}$C–CO$_2$Me]$^-$ anion, illustrating the atom labelling and the angles that were taken as variables in the van der Waals energy calculations.
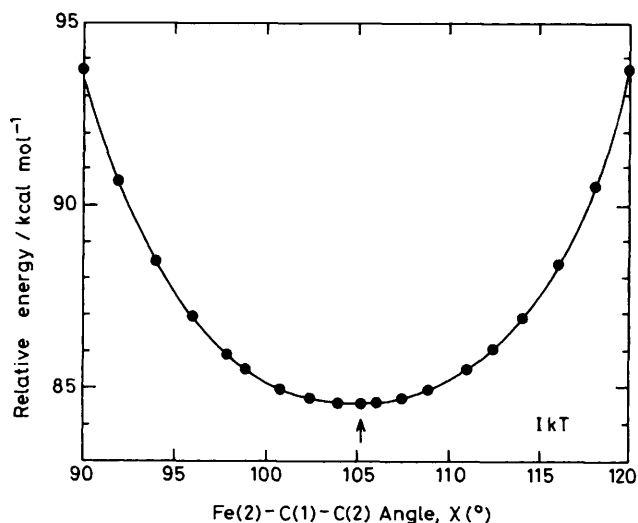

Figure 2. The total relative van der Waals energy calculated as a function of the tilting of the ester function, χ (1 cal = 4.184 J). In the crystal structure χ is found to be 105.3° (indicated by the arrow).[4]

optimising the value of the rotation about the C(1)–C(2) bond, views of the cluster plotted using full van der Waals radii indicate considerable overlap between the methyl protons and the carbonyl functions. This graphical indication is substantiated on computing the van der Waals energy sum which is more than 50 kT higher for the ethylidyne (R = Me) case than for the vinylidene (R = CH_2). Our simple modelling thus indicates that an sp^3 hybridised substituent will not be accommodated at C(2) without reorganisation of the cluster unless there are favourable bonding effects to counteract this nonbonding energy debit. However, a molecular orbital study of (1) has revealed substantial $p\pi$ overlap between C(2) and C(1).[1] The destabilisation of the sp^3 hybridised substituent at C(2) that derives from the steric crowding in the cluster is thus complemented by bonding effects that favour those derivatives that have sp^2-hybridisation at C(2). Indeed, although the synthetic efforts of several groups have resulted in the characterisation of a wide variety of substituted iron butterfly clusters, such as R = CO_2Me^-,[4] $C(O)Me^-$,[7] $C(OMe)_2$,[8] $C(Me)OMe$,[8] and $CHMe$,[9] every one of these has sp^2 hybridisation geometry at the carbido substituent.

Although workable force-fields are not yet available for the majority of organometallic cluster constituents, the steric constraints in such systems often derive from the ligand–ligand nonbonded interactions. Interactive molecular graphics provides a simple means of probing such interactions both visually and by semi-quantitative nonbonded interaction energy calculations. This is a new area for application of the technique,[10] and one which we anticipate has considerable scope.

References

1 S. D. Wijeyesekera, R. Hoffman, and C. N. Wilker, *Organometallics*, 1984, **3**, 962.

2 S. Harris and J. S. Bradley, *Organometallics*, 1984, **3**, 1086.

3 Three specialist journals now incorporate a large interactive molecular graphics content and provide access to the recent literature: *Journal of Molecular Graphics* (Molecular Graphics Society, Butterworth, London); *Journal of Computational Chemistry* (Wiley, New York); *Computers and Chemistry* (Pergamon, New York).

4 J. S. Bradley, G. B. Ansell, and E. W. Hill, *J. Am. Chem. Soc.*, 1979, **101**, 7417.

5 G. Del Re, E. Gavuzzo, E. Giglio, F. Lelj, F. Mazza, and V. Zappia, *Acta. Crystallogr., Sect. B*, 1977, **33**, 3289.

6 CHEMGRAF program suite (1982): © E. K. Davies, Chemical Crystallography Laboratory, University of Oxford.

7 J. H. Davis, M. A. Beno, J. M. Williams, J. Zimmie, M. Tachikawa, and E. L. Muetterties, *Proc. Natl. Acad. Sci. USA*, 1981, **78**, 668.

8 J. S. Bradley, *Philos. Trans. R. Soc. London, Ser. A*, 1982, **308**, 103.

9 J. S. Bradley, E. W. Hill, and C. S. Day, unpublished work.

10 J. M. Newsam and T. R. Halbert, *Inorg. Chem.*, 1985, **24**, 491.