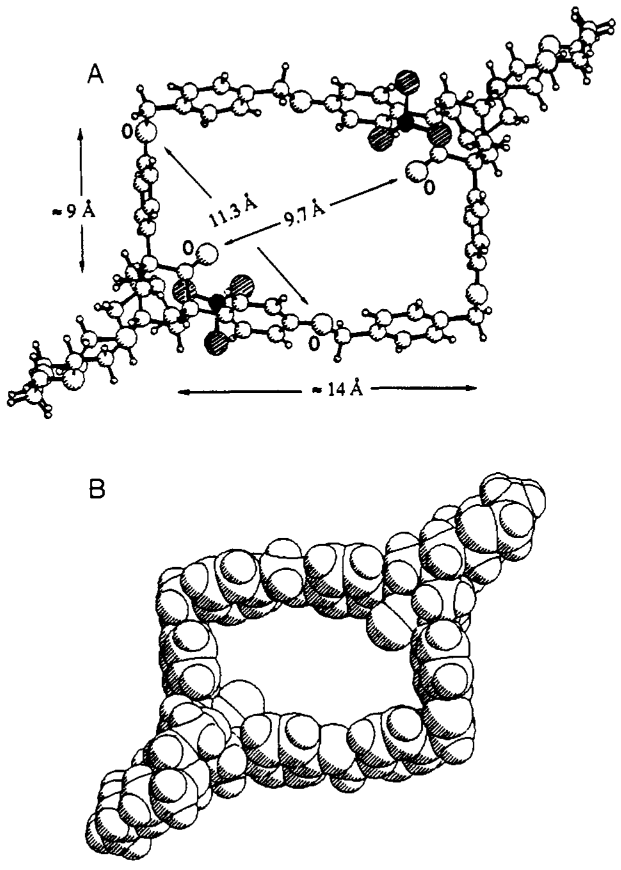


Figure 1. (A) X-ray crystal structure of cyclophane **1** showing selected interatomic distances and the two localized chloroform molecules. (B) Space-filling representation of the X-ray crystal structure of **1**.

is solvated by a pool of highly disordered chloroform molecules which, except for two, could not be located (Figure 1A).

The effect of the intracavity functional groups in **6**–**8** on the stability of 1:1 inclusion complexes was investigated by ^{1}H NMR titrations in 0.8 M DCl in D_2O/CD_3OD (60:40, % v/v) at 293 K with [host] = 5×10^{-4} M and [6-cyano-2-naphthol] = (1–12) $\times 10^{-3}$ M. In these titrations, the complexation-induced upfield shifts ($\Delta\delta_{sat} \approx 0.5$–1.0 ppm) of the methylene protons in the *n*-butyl bridges of the hosts were evaluated. Macrocycle **8** with no intracavity functional group is by far the best receptor in the series (K_a = 205 L mol^{-1}, $\Delta G°$ = −3.1 kcal mol^{-1}). Ketone **6** forms a weaker complex (K_a = 40 L mol^{-1}, $\Delta G°$ = −2.2 kcal mol^{-1}), whereas the hydroxy derivative **7** does not exhibit any significant binding ($K_a \ll 10$ L mol^{-1}, $\Delta G° \gg -1.3$ kcal mol^{-1}). The observed differences in $\Delta G°$ ($\geq$2 kcal mol^{-1}) reflect specific desolvation effects. In the cavities of **6** and **7**, incorporation of an apolar naphthalene residue leads to the energetically unfavorable desolvation of the strongly solvated intracavity functional group. Functional group transformations leading to receptors with convergent, precisely located intracavity catalytic residues are now being pursued.

Acknowledgment. This work was supported by the National Science Foundation.

Registry No. 1, 138434-67-0; **2** precursor, 138434-81-8; **2**, 138434-68-1; **3**, 138434-69-2; **4**, 138434-70-5; **5**, 138434-71-6; **6** precursor, 138434-82-9; **6**, 138434-72-7; **7** precursor, 138434-83-0; **7**, 138434-73-8; **8** precursor, 138434-84-1; **8**, 138434-74-9; **9**, 29903-09-1; **10**, 138434-75-0; **11**, 138434-76-1; **12**, 138434-77-2; **13**, 138434-78-3; **14**, 138434-79-4; **15**, 138434-80-7; HCHO, 50-00-0; $TosO(CH_2CH_2CH_2O)_3Tos$, 19249-03-7; 2-aminoethanol, 141-43-5; 1,4-dichlorobutane, 110-56-5; *p*-xylylene dichloride, 623-25-6; *p*-xylylene dibromide, 623-24-5; 1,2-ethylenediamine, 107-15-3; 6-cyano-2-naphthol, 52927-22-7.

Supplementary Material Available: Experimental details of the X-ray crystal structure analysis, fully labelled view of the structure, and tables of atomic coordinates, equivalent isotropic thermal parameters, bond angles, and bond lengths for **1** (7 pages); table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Eclipsed Conformations of 1,1,2-Trisubstituted Single Bonds with Space-Demanding Substituents. Examples from X-ray Diffraction Structure Determinations

J. E. Anderson*

Chemistry Department, University College
Gower Street, London WC1E 6BT, United Kingdom

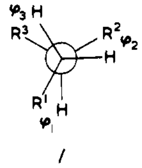
D. G. Watson

Cambridge Crystallographic Data Centre
Lensfield Road, Cambridge CB2 1EW, United Kingdom

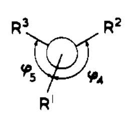
Received October 28, 1991

Recently one of us showed that the preferred conformation along the central bond of 1,1,2-tri-*tert*-butylethane is near to eclipsed[1] and postulated that the central bond in any molecular fragment $R^1X\text{-}\text{-}\text{-}YR^2R^3$ (involving tetrahedral atoms X = CH_2, NH, O, etc., Y = CH, N, etc., and groups R demanding of space) should show a similar tendency. We now report our success in verifying the postulate often with simpler groups R, using known structures in the Cambridge Crystallographic Data Base.

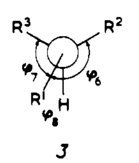
We define an eclipsing sum Σ as the sum of the arithmetic values of the three smaller dihedral angles involving the C–R bonds, i.e., $|\phi_1| + |\phi_2| + |\phi_3|$ in diagram **1**. For a perfectly staggered conformation, Σ is 180°, and for a conformation with all bonds perfectly eclipsed,[2] Σ is 0°. Perfect eclipsing of all groups on a bond with freedom to rotate is unlikely due to other distortions, so we will use the term "nearly eclipsed" if Σ is less than 60° and "eclipsed" if Σ is less than 30°, in which case average dihedral angles are less than 10°.



1



2



3

Where hydrogen atoms are not identified explicitly in the structure determination, a pseudoeclipsing sum $\psi\Sigma$ can be defined. Thus when only two dihedral angles are identified, as shown in **2**, $\psi\Sigma$ is $1.5 \times [|(120 - |\phi_4|)| + |(120 - |\phi_5|)|]$. Where three dihedral angles are identified, as shown in **3**, $\psi\Sigma$ is $|(120 - |\phi_6|)| + |(120 - |\phi_7|)| + |\phi_8|$.

We found no crystal structures with fragments of the type $CH_3CH_2\text{-}\text{-}\text{-}CH(CR_3)CR_3$ (**4a**) or $R_2CHCH_2\text{-}\text{-}\text{-}CH(CR_3)CR_3$ (**4b**) [groups R ($\neq$H) need be neither alkyl groups nor identical]. Fifteen structures were found, however, containing the structural fragment $RCH_2CH_2\text{-}\text{-}\text{-}CH(CR_3)CR_3$ (**5**). In 12 cases[3a-k] arising

---

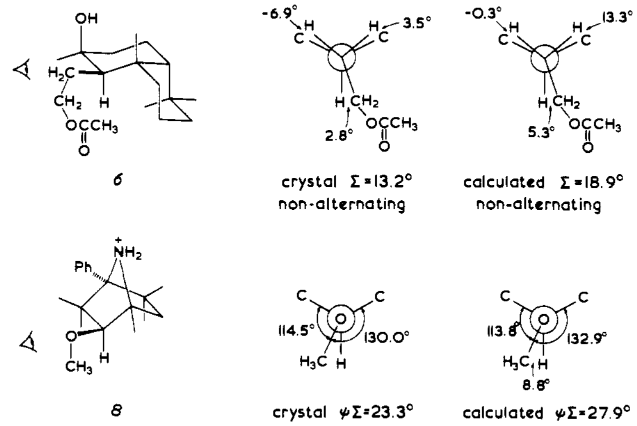
[1] Anderson, J. E. *J. Chem. Soc., Perkin Trans. 2* **1991**, 299.

[2] We are aware that perfect eclipsing is no different from eclipsing and that bonds not perfectly eclipsed are not eclipsed at all, pedantically.

[3] (a) Escher, S.; Giersch, W.; Niclass, Y.; Bernardinelli, G.; Ohloff, G. *Helv. Chim. Acta* **1990**, *73*, 1935. (b) Bernardinelli, G.; Vial, C.; Starkemann, S.; Naf, F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1988**, *44*, 715. (c) Bjamer, K.; Ferguson, G.; Melville, R. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *24*, 855. (d) Tanaka, R.; Matsunaga, S.; Ishida, T.; Shingu, T. *Tetrahedron Lett.* **1989**, *30*, 1661. (e) Bernardinelli, G.; Giersch, W. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41*, 746. (f) Rodriguez, M. L.; Martin, J. D.; Estrada, D. *Acta Crystallogr., Sect. C: Cryst. Commun.* **1989**, *45*, 306. (g) Bernardinelli, G.; Dunand, A.; Flack, H. D.; Yvon, K.; Giersch, W.; Ohloff, G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *40*, 1911. (h) Schmitz, F. J.; Hollenbeak, K. H.; Carter, D. C.; Hossain, M. B. *J. Org. Chem.* **1979**, *44*, 2445. (i) Smith-Verdier, P.; Florencio, F.; Garcia-Blanco, S. *Cryst. Struct. Commun.* **1979**, *8*, 537. (j) Caccamese, S.; Toscano, R. M.; Cerrini, S.; Gavuzzo, E. *Tetrahedron Lett.* **1982**, *23*, 3415. (k) Begley, M. J.; Cheshire, D. R.; Harrison, T.; Hutchinson, J. H.; Myers, P. L.; Pattenden, G. *Tetrahedron* **1989**, *45*, 5215.

0002-7863/92/1514-1517$03.00/0

Scheme I



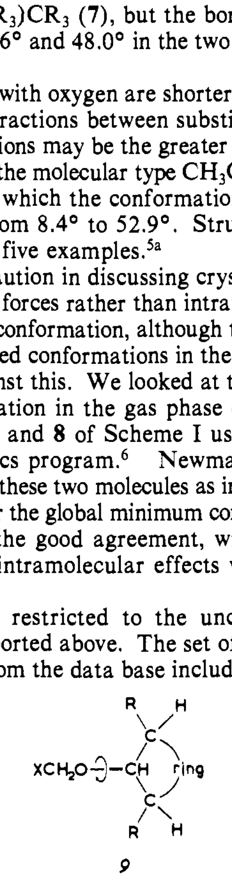
from a 2,2,6,6-tetrasubstituted cyclohexane ring, the bond was more or less eclipsed, with Σ varying from 13.2° to 48.0°. Scheme I shows structure **6** with the smallest of these Σ values.[3a]

Only one structure was found[4] with a fragment of the type CR_3CH_2- - -$CH(CR_3)CR_3$ (**7**), but the bond is nearly eclipsed, with Σ values of 33.6° and 48.0° in the two molecules in the unit cell.

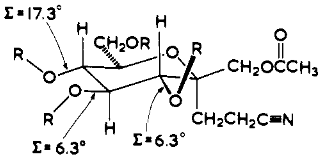
Bonds of carbon with oxygen are shorter than carbon–carbon bonds, and the interactions between substituents which lead to eclipsing conformations may be the greater therefore. We found five examples[5a–e] of the molecular type CH_3O- - -$CH(CR_3)_2$ in the data base, in all of which the conformation is near to eclipsed, with ψΣ ranging from 8.4° to 52.9°. Structure **8** in Scheme I shows one of these five examples.[5a]

It is a point of caution in discussing crystal structure conformations that lattice forces rather than intramolecular strain may be determining the conformation, although the consistency of the occurrence of eclipsed conformations in the two sets of examples quoted argues against this. We looked at this further by calculating the conformation in the gas phase of the two relatively simple molecules **6** and **8** of Scheme I using Allinger's MM3 molecular mechanics program.[6] Newman projections of the significant bond for these two molecules as in the crystal structure and as calculated for the global minimum conformation are shown in Scheme I, and the good agreement, within 5° on average, suggests that it is intramolecular effects which determine the eclipsing.

Eclipsing is not restricted to the uncommonly branched structural types reported above. The set of 25 molecules of the structural type **9** from the data base includes 16 molecules with at least one eclipsed or nearly eclipsed bond, seven of these involving at least one bond with an eclipsing sum of less than 30°. It is not appropriate to examine this more miscellaneous range in a brief communication, but structure **10** shows a simple molecule with several eclipsed bonds.[7a]



9



10 R = CH_2Ph

This last is one of several examples of a particularly simple type which promises to be a rich source of eclipsed conformations. When there are three adjacent equatorial substituents on a six-membered ring, the middle one being $-X-CH_3$ (or of course $-X-CR^aR^bR^c$), the flanking groups will push the central bond conformation toward one with the $X-CH_3$ bond eclipsing the ring-H bond.

The presence of an eclipsed single bond conformation was noted explicitly in only one of the 34 crystal structure determination reports referred to here, and the importance of vicinal interactions of groups R was in fact suggested.[7b] The number of examples and the relative simplicity of some of them strengthen the original postulate.[1,8]

Acknowledgment. We are grateful to the Ramsay Memorial Fellowships Trust for bringing together this problem and its solution.

---

[4] Shiomi, K.; Nakamura, H.; Iinuma, H.; Naganawa, H.; Takeuchi, T.; Umezawa, H.; Iitaka, Y. *J. Antibiot.* **1987**, *40*, 1213.

[5] (a) Swanson, R.; Stavinova, J. L.; Mariano, P. S. *Cryst. Struct. Commun.* **1982**, *11*, 799. (b) Mazzocchi, P. H.; Somich, C.; Ammon, H. *Tetrahedron Lett.* **1984**, *25*, 3551. (c) Somich, C.; Mazzocchi, P. H.; Ammon, H. L. *J. Org. Chem.* **1987**, *52*, 3614. (d) Miyahara, K.; Kawasaki, T.; Kinjo, J.-E.; Shimokawa, T.; Yamahara, J.; Yamasaki, M.; Harano, K.; Nohara, T. *Chem. Pharm. Bull.* **1986**, *34*, 4166. (e) Bokii, N. G.; Yanovskii, A. I.; Yu, T.; Struchkov, T.; Shemyakin, N. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, *95*, 380.

[6] Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551. Because of limitations in the parametrization, the calculation reported for **8** is in fact for the compound without the remote phenyl group.

[7] (a) Giese, B.; Dupuis, J.; Leising, M.; Nix, M.; Lindner, H. J. *Carbohydr. Res.* **1987**, *171*, 329. (b) Luger, P.; Paulsen, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *37*, 1693.

[8] Anderson, J. E. Conformational Analysis of Acyclic and Alicyclic Saturated Hydrocarbons. In *The Chemistry of Alkanes and Cycloalkanes*; Patai, S., Ed.; Wiley: Chichester, Chapter 3.II.D, in press.

Transition Metal Complexes Containing Donor-Stabilized Silylyne Ligands. Reductive Dimerization to a Silylene Complex

Steven D. Grumbine, Raj K. Chadha, and T. Don Tilley*

Department of Chemistry, 0506
University of California at San Diego
9500 Gilman Drive, La Jolla, California 92093-0506

Received November 1, 1991

Recent progress in the synthesis of transition metal complexes with unsaturated silicon ligands has stimulated interest in development of new transition metal–silicon chemistry.[1,2] In particular, attention has focused on silylene complexes,[1a–c,j,k] which we have obtained via silyl complexes possessing a labile triflate group.[2] For example, $Cp^*(PMe_3)_2RuSi(STol\text{-}p)_2(OTf)$ (Cp^* = $\eta^5\text{-}C_5Me_5$; OTf = OSO_2CF_3) dissociates triflate in solution to give $Cp^*(PMe_3)_2Ru{=}Si(STol\text{-}p)_2^+$.[2b] Availability of the bis(triflate) derivative $Cp^*(PMe_3)_2RuSi(STol\text{-}p)(OTf)_2$ (**1**),[2b] and its ionization in acetonitrile,[3] suggested possible routes to new silylene

---

[1] Leading references: (a) Probst, R.; Leis, C.; Gamper, S.; Herdtweck, E.; Zybill, C.; Auner, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1132. (b) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415. (c) Corriu, R.; Lanneau, G.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1130. (d) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 4079. (e) Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517. (f) Berry, D. H.; Chey, J.; Zipin, H. S.; Carroll, P. J. *Polyhedron* **1991**, *10*, 1189. (g) Koloski, T. S.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1990**, *112*, 6405. (h) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1991**, *113*, 1870. (i) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068. (j) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415. (k) Tilley, T. D. In *The Silicon–Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapter 10, p 309.

[2] (a) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673. (b) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801.