surface oxide was stripped with concentrated HCl, to provide an arsenic-covered surface,[15,16] rinsed with pure water, and immediately placed in N_2-purged PTFE containers with enough ODT (Aldrich; recrystallized, mp 29.5–31.0 °C) to cover the wafer after the thiol melted. Heating at 100 °C for 5 h gives good quality monolayers; shorter reaction times or lower temperatures lead to incomplete, disordered monolayers. After extensive solvent (chlorobenzene, ethanol, water) washing the films were analyzed. Contrary to the observation with the Au system,[6] similar processing but with dialkyl disulfide does not result in monolayer formation.

Single-wavelength ellipsometry[4,8a] showed the films to have a reproducible thickness of 14 ± 2 Å. The transmission and reflection (55° angle of incidence, p-polarization) infrared spectra (2-cm^{-1} resolution) of the monolayer sample (Figure 1) show that the symmetric and antisymmetric CH_2 stretching modes are peaked at 2850 (transmission) and 2848 (reflection), and 2919 (transmission) and 2916 cm^{-1} (reflection), respectively. These frequencies strongly indicate a densely packed assembly of rodlike chains with a low degree of gauche defects.[8a,9d,17] When anisotropic (tensor) optical functions[9d,18] determined from crystalline $(C_{18}H_{37}S)_2$ are used, spectral simulations made for a 14-Å film show a best fit (Figure 1) to experiment[19] for an average chain tilt of 57 ± 3° from the surface normal with a chain twist of 45 ± 5°. For a fully extended chain structure of 26-Å chains the ellipsometric data give an average tilt of 57 ± 3°. The inset in Figure 1 shows the approximate configuration of the octadecyl chains as seen looking at a plane perpendicular to the surface and containing the chain. For $\theta = 57°$ the interchain spacing a in Figure 1 is 8 Å.[20]

High coverage of the surface by alkyl groups is evident from the oleophobic character of the surface, demonstrated by the observation of a contact angle (static pendant drop) of hexadecane equal to 41 ± 2°. In comparison, the densely packed films made from adsorption of $C_{18}H_{37}SH$ on Cu, Ag, and Au[9d] and of $C_{18}H_{37}SiCl_3$ on native SiO_2[21] show reported angles of 46° and 43°, respectively.[22]

A comparison of the X-ray photoelectron spectra[23] for a GaAs (100) substrate with native oxide (10 Å), an oxide-stripped surface, and an ODT monolayer stored in air for over 2 days shows that the ODT films impart a significant stability toward oxidation of the GaAs as evidenced by the significant drop in the intensities of the As 3d (45 eV) peak associated with oxide and the O 1s peak (532 eV) in the thiol-treated sample (we estimate less than about 3% of a monolayer of oxide even after the 2-days exposure). It has been shown by Sandroff and co-workers[24] that S–As bonds form as a result of aqueous sulfide ion treatment of the GaAs (100) surface, but even at the resolution of our measurements,[23] because of intrinsic line widths, the S 2p peak (165 eV) overlaps the Ga 3s peak (160 eV), precluding detailed interpretation of the interfacial bonding.[25] We note that the sulfide ion treated surfaces are not very stable toward oxidation.

From the point of view of potential chemical sensor applications, it is extremely important to note that we find, as with Au,[6,8d,26] a variety of functionalized surfaces can be prepared from $X(CH_2)_nSH$, where X is a common functional group such as OH, CO_2CH_3, and CO_2H. For example, for $X = CO_2H$ and $n = 15$ the resultant surface shows a pH-dependent contact angle curve which is qualitatively similar to that reported[27] for the film on Au, with an inflection point at about pH = 6.

Further studies on the structural chemical and electrical[28] aspects of these films are in progress and will be reported elsewhere.

Acknowledgment. We gratefully acknowledge C. J. Sandroff for valuable discussions and D. Angst for assistance in obtaining the XPS data. Support for this work was provided by the Army Research Office and the National Science Foundation (DMR-900-1270).

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[15] Sze, S. M. *Semiconductor Devices Physics and Technology*; J. Wiley: New York, 1985.

[16] During transport into the purged reaction vessel, a very minor regrowth of surface oxide can be expected.

[17] Snyder, R. G.; Strauss, H. L.; Elliger, C. A. *J. Phys. Chem.* **1982**, *86*, 5145–5150. Snyder, R. G.; Maroncelli, M.; Strauss, H. L.; Hallmark, V. M. *J. Phys. Chem.* **1986**, *90*, 5623–5630.

[18] Parikh, A. N.; Allara, D. L. *J. Chem. Phys.*, in press.

[19] The transmission experiment was simulated. The reflection experiment was not because of interference effects associated with the two-sided, parallel-face samples (optical cavity effects). However, the spectral peak frequencies are unaffected. Note that the simulated line widths are several wavenumbers less than the experimental, which suggests some subtle differences in chain structure between the monolayer and the bulk crystalline disulfide phase. Exploration of the details of the vibrational spectra are in progress.

[20] This structure is reasonably self-consistent on the basis of chemical bonding of the chains to a fixed As lattice with the tilt angles of the chains adjusting to achieve maximum packing. The lattice constant for the *fcc* zincblende crystal of GaAs is 5.63 Å. Given the 4.5-Å chain diameter, the first regular lattice upon which chains can fit on the (100) surface has first and second nearest neighbor spacings of 5.63 and 7.98 Å, respectively. Tilting of the chains exclusively along each of these two directions yields tilt angles of ~37° and 56°, respectively. The experimental results suggest tilting predominantly along the diagonal (7.98 Å) direction. However, some rotation of alignment toward the nearest neighbor direction is expected in order to maximize chain overlap. In-plane X-ray diffraction experiments are in progress to provide definitive structures.

[21] Wasserman, S. R.; Tao, Y. T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074–1087.

[22] Lower values might be expected for the $\theta = 57°$ monolayer because of the partial CH_2 character of the surface (see Figure 1 inset).[5b]

[23] Measurements were made using monochromatic Al Kα radiation and an instrument resolution of 500 meV. Under the conditions of a typical measurement, no degradation of the films was observed.

[24] Sandroff, C. J.; Hedge, M. S.; Chang, C. C. *J. Vac. Sci. Technol., B* **1989**, *7*, 841–844.

[25] Presumably RS–As bonds form. Preliminary IR analysis of odd–even chain structures provide evidence for a fixed surface–S–C bond angle of ~90°. The occupation of alternating As atoms required by the 5.63-Å lattice together with the high $RSH/(RS)_2$ reactivity ratio suggests that the unoccupied As atoms are capped by H atoms.

[26] Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558–569.

[27] Troughton, E. B.; Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *4*, 365–385.

[28] Nakagawa, O.; Sheen, C. W.; Ashok, S.; Allara, D. L. submitted for publication.

Water-Soluble Cyclophane Receptors with Convergent Functional Groups

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During the past decade, we and others have prepared cyclophane receptors with apolar cavities which form stable inclusion complexes with apolar solutes in aqueous solution.[1] Here, we describe a new series of water-soluble cyclophanes featuring carbonyl or hydroxyl residues converging in a precise geometrical array into large apolar binding cavities.[2]

Schemes I and II show the short syntheses of the eight cyclophanes **1–8** via the novel spacers **11–14**.[3,4] In protonated form,

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[1] (a) Diederich, F. *Cyclophanes, Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, 1991; Vol. 2. (b) Vögtle, F. *Supramolekulare Chemie*; Teubner: Stuttgart, 1989. (c) Odashima, K.; Koga, K. In *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; Vol. 2, pp 629–678.

[2] (a) Rebek, J., Jr. *Angew. Chem.* **1990**, *102*, 261–272; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 245–255. (b) Hamilton, A. D. *J. Chem. Educ.* **1990**, *67*, 821–828. (c) Wilcox, C. S. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Dürr, H., Eds.; VCH: Weinheim, Germany, 1991; 123–143. (d) Sheridan, R. E.; Whitlock, H. W., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7120–7121. (e) Hong, J.-I.; Namgoong, S. K.; Bernardi, A.; Still, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 5111–5112. (f) Askew, B. C. *Tetrahedron Lett.* **1990**, *31*, 4245–4248. (g) Bonar-Law, R. P.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1991**, 574–577. (h) Davis, A. P.; Orchard, M. G.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 612–614.

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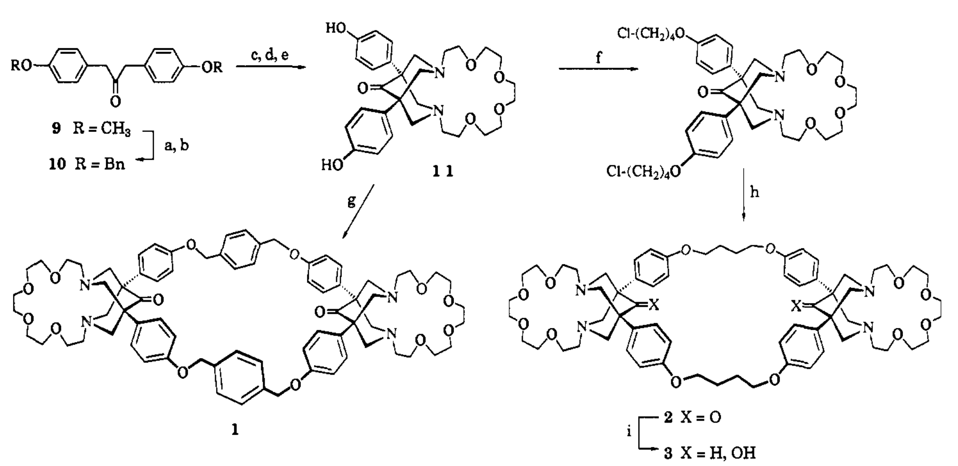
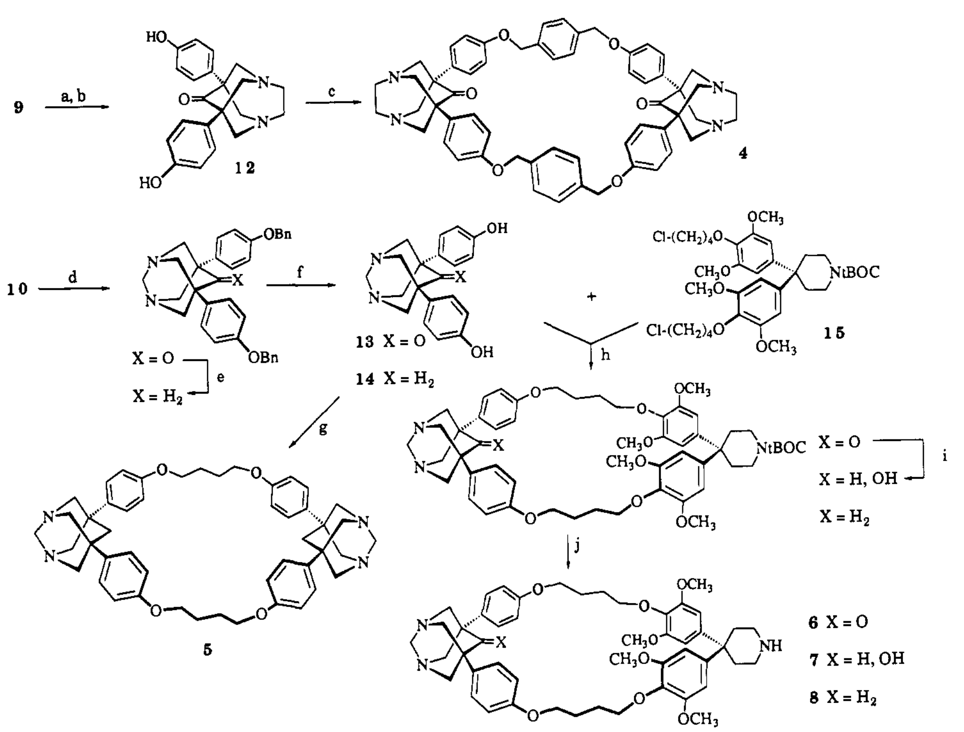
Scheme I[a]



[a] Reagents and yields: (a) HBr, HOAc, reflux; 95%. (b) Benzyl bromide, K_2CO_3, acetone, reflux; 87%. (c) HCHO, 2-aminoethanol, HOAc/EtOH, reflux; 37%. (d) NaH, $TosO(CH_2CH_2O)_3Tos$, THF, high dilution, reflux; 63%. (e) HCO_2NH_4, 10% Pd/C, acetone, reflux; 73%. (f) NaH, 1,4-dichlorobutane, DMF, 20 °C; 99%. (g) *p*-Xylylene dichloride, Cs_2CO_3, CH_3CN, high dilution, reflux; 14%. (h) 1 equiv of **11**, Cs_2CO_3, DMF, high dilution, 80 °C; 18%. (i) $LiAlH_4$, THF, 20 °C; 68%.

Scheme II[a]



[a] Reagents and yields: (a) HCHO, 1,2-ethylenediamine, HOAc/EtOH, reflux; 61%. (b) HI, HOAc, reflux; 88%. (c) NaH, *p*-xylylene dibromide, DMF, high dilution, 20 °C; 7%. (d) HCHO, $CH_3CO_2NH_4$, EtOH, reflux; 78%. (e) $N_2H_4{\cdot}H_2O$, CH_3CO_2Na, $HO(CH_2)_2O(CH_2)_2OH$, reflux, then HCHO, MeOH, reflux; 99%. (f) HCO_2NH_4, 10% Pd/C; for **13**, THF, reflux (88%); for **14**, DMF, 50 °C (88%). (g) Cs_2CO_3, 1,4-dichlorobutane, DMF, high dilution, 55 °C; 6%. (h) Cs_2CO_3, DMF, high dilution, 55 °C; 13% (X = O and X = H_2). (i) $LiAlH_4$, THF, 20 °C; 82%. (j) CF_3CO_2H, CH_2Cl_2, 20 °C; 86% (**6**), 74% (**7**), 52% (**8**).

macrocycles **3** and **6–8** show the highest monomer solubility in 1.5 M DCl in D_2O/CD_3OD (60:40, % v/v); their critical aggregation concentrations were determined by ^1H NMR as CAC $> 3 \times 10^{-3}$ M. Under the same conditions, systems **1** (CAC $\approx 1 \times 10^{-4}$ M) and **2** (CAC $\approx 5 \times 10^{-4}$ M) are much less soluble. Compound **5** is soluble in 1.5 M DCl in D_2O/CD_3CN (60:40, % v/v) with CAC $\approx 7 \times 10^{-4}$ M, whereas attempts to dissolve **4** in various acidic aqueous solutions failed.

Crystallization of the tritopic receptor **1** from chloroform yielded crystals suitable for X-ray analysis (Figure 1).[5] The interior of the large preorganized cavity with two convergent keto groups

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(3) All new compounds provided satisfactory spectroscopic and analytical data. Carbamate **15** was prepared by reaction of 4,4-bis(4-hydroxy-3,5-dimethoxyphenyl)piperidine with BOC anhydride followed by alkylation with 1,4-dichlorobutane. Macrocycle **3** was characterized as a mixture of two isomers.

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(5) X-ray crystal data for **1** ($C_{74}H_{88}N_4O_{14}{\cdot}2CHCl_3$): M_r = 1496.3; monoclinic; space group $P2_1/n$; Z = 2; a (Å) = 13.424 (3); b (Å) = 15.735 (3); c (Å) = 18.280 (3); β = 95.533 (5)°; V (Å^3) = 3843. Data were collected on a Syntex diffractometer using Cu Kα radiation, $2\theta \leq 100°$, giving 3954 unique reflections; the structure was solved by statistical methods (SHELX86), yielding R = 0.143 and R_w = 0.141 for 1180 reflections with $I > 3\sigma(I)$.

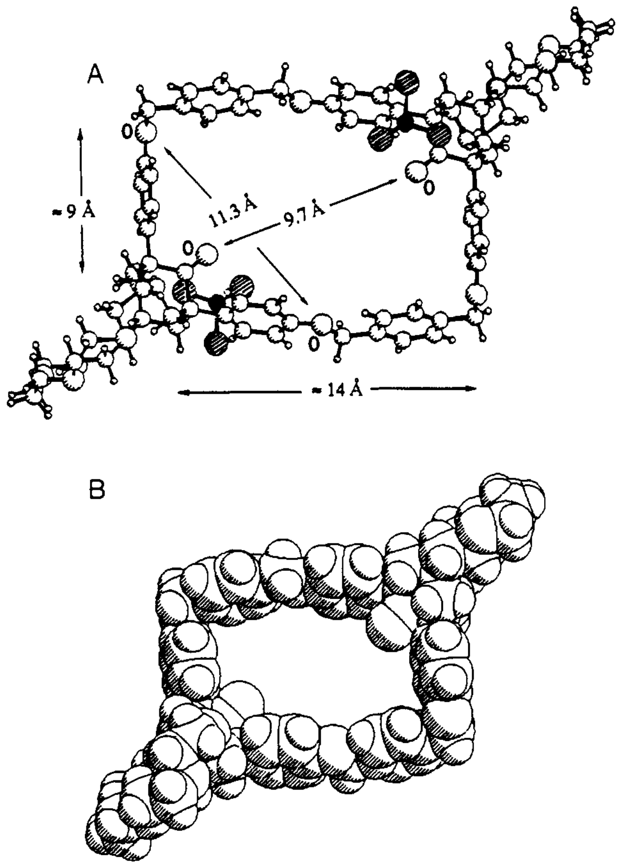

Figure 1. (A) X-ray crystal structure of cyclophane **1** showing selected interatomic distances and the two localized chloroform molecules. (B) Space-filling representation of the X-ray crystal structure of **1**.

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 $\Delta G°$ (≥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

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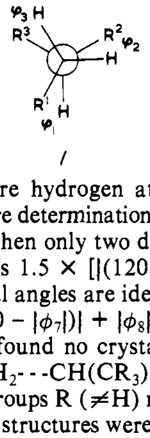
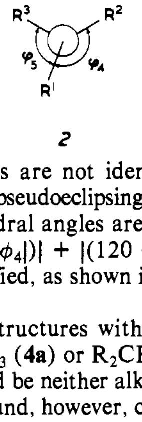
Recently one of us showed that the preferred conformation along the central bond of 1,1,2-tri-*tert*-butylethane is near to eclipsed[1] and postulated that the central bond in any molecular fragment R^1X- - -YR^2R^3 (involving tetrahedral atoms X = CH_2, NH, O, etc., Y = CH, N, etc., and groups R demanding 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



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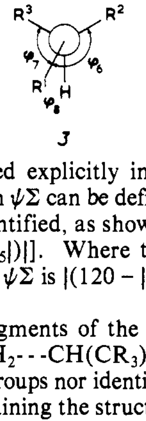

3

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- - -$CH(CR_3)CR_3$ (**4a**) or R_2CHCH_2- - -$CH(CR_3)CR_3$ (**4b**) [groups R (≠H) need be neither alkyl groups nor identical]. Fifteen structures were found, however, containing the structural fragment RCH_2CH_2- - -$CH(CR_3)CR_3$ (**5**). In 12 cases[3a–k] arising

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[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.

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