

9 followed by Wittig reaction with the triphenylphosphorane¹² derived from methyl 4-bromocrotonate gave the diene **10**, and removal of the isopropylidene group (MeOH/*p*-TsOH) then produced the crystalline (*E,E*)-dihydroxyester **16** (mp 84–86 °C) in 53% yield from **8**.¹³

An alternative procedure leading to the carbon skeleton of **8** with the correct configuration was also developed from diethyl (*S*)-malate via the benzylidene acetal **11**.^{6b} Chain extension using the triflate **12** gave the cyanide **13**, which could be converted to the lactone **14**. This lactone can be methylated with high diastereoselectivity to give **15** in 30% overall yield from **11**.¹⁴ A method for the conversion of **15** to **8** is currently being sought.

The preparation of the dialdehyde **21** was achieved as follows. Selective protection of the primary hydroxyl group of **16** (tritylpyridinium tetrafluoroborate/MeCN, 20 °C, 1 h)¹⁵ gave **17** (mp 120.5–121 °C), and subsequent hydrolysis of the methyl ester (KOH/MeOH/THF, 16 h, 20 °C) then gave the seco-acid **18**. Dimerization of **18** was accomplished by Yamaguchi's procedure⁷ to give the diolide **19**, which was then converted (MeOH/*p*-TsOH) to the diol **20** (mp 186–188 °C). Finally Swern¹¹ oxidation produced the dialdehyde **21**¹⁶ (29% yield from the dihydroxyester **16**, and 8.7% overall from the aldehyde **5** over 13 steps).

Earlier studies on the ketone **25**, unprotected at C-5, indicated that it was very unstable¹⁷ (Chart III). We therefore reasoned that two different protecting groups would be required at C-5 and C-7 to ensure that in the final step the free β -hydroxy ketone function would not be exposed. Selective removal of the C-7 hydroxyl protective group should permit the cyclization to a δ -lactol which would then not be so prone to elimination. The aldol derivative **25** was prepared as follows. Treatment^{6b} of ethyl (*R*)-3-hydroxybutyrate **4**^{6c} with 2 equiv of LDA and 3 equiv of EtI (–40 °C, 16 h) gave the ester **22** as the only product. The hydroxyl group of **22** was protected to give the triethylsilyl ether **23**, which was converted over two steps (DIBALH, –60 °C and Swern oxidation) to the aldehyde **24** (67% overall yield from **4**). Mukaiyama reaction between the aldehyde **24** and 2-[(trimethylsilyloxy)-1-butene (2 equiv) (TiCl₄/CH₂Cl₂, –78 °C, 5 min) gave a *single* unstable aldol¹⁵ which could be protected (*tert*-butyldimethylsilyl chloride/imidazole) to give **25** (16% from **24**). Methanolysis of **25** led to the 2-methoxy-4-hydroxypyran **26**,¹⁹ a reaction that served as a model for the final step in the total synthesis of **1c**.

Treatment of the ketone **25** with dibutylboron triflate and diisopropylethylamine²⁰ gave a single *Z*-boron enolate enolized toward C-2 (confirmed by reaction of the enolate with benz-

aldehyde). Reaction of 4 equiv of this enolate with the dialdehyde **21** (Et₂O/CH₂Cl₂, –78 °C, 1 h; 0 °C, 30 min) gave, after oxidative workup (HMPT-py-MoO₅), **27a**, **27b**, and **27c** (3:5:6, 42% combined yield) as the *only* isolable aldol adducts, which were easily separable by flash chromatography. Treatment of **27a** with MeOH/*p*-TsOH gave the aglycone **1c** of elaiophylin (17%) identical by 300-MHz ¹H NMR, IR, [α]_D, and TLC with our sample prepared from elaiophylin.^{5,21}

Experiments to improve the yields of the last two steps are underway. Once we have converted the lactone **15** to the alcohol **8**, a unique feature in our macrolide synthesis will be that all but two (C-9 and C-10) of the asymmetric carbon atoms will have been derived solely from "chiral pool" starting materials with only one asymmetric carbon atom (formally by 1,2-asymmetric inductions).²²

(21) Satisfactory ¹H NMR, IR, MS, and microanalyses were obtained for all stable, crystalline, or distillable compounds.

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Design of Molecular Assembly of Diphenylcarbenes Having Ferromagnetic Intermolecular Interactions

Tadashi Sugawara, Shigeru Murata, Keisaku Kimura, and Hiizu Iwamura*

Division of Applied Molecular Science
Institute for Molecular Science, Okazaki 444, Japan

Yoko Sugawara and Hitoshi Iwasaki

Riken (The Institute of Physical and
Chemical Research), Wako, Saitama 351-01, Japan
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Molecular design of organic ferromagnets is the current topic of interest in organic material science.¹ Some high-spin hydrocarbons were found to behave as superparamagnets and can be regarded as "micro" domains in ferromagnets.² Therefore introduction of ferromagnetic intermolecular (interdomain) interaction is expected to lead to macroscopic ferromagnetism.³ We wish to propose here one of the strategies for designing an assembly of carbene molecules which may display macroscopic magnetic properties. We have taken advantage of the dispersion force of alkyl chains,⁴ and have introduced octyloxy groups at the para positions of diphenyldiazomethane to realize a favorable orientation and overlap in the resulting carbene species in crystals.⁵ The ESR spectrum of the photolyzate of polycrystalline bis[*p*-(octyloxy)-phenyl]diazomethane (**1**) at 10 K showed a complex multiplet

(1) (a) Iwamura, H.; Sugawara, T.; Itoh, K.; Takui, T. *Mol. Cryst. Liquid Cryst.* **1985**, *125*, 251. (b) Breslow, R. *Ibid.* **1985**, *125*, 261. (c) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786.

(2) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1984**, *106*, 6449.

(3) Sugawara, T.; Tukada, H.; Murata, S.; Iwamura, H., to be published elsewhere. The crystals of diphenyldiazomethanes carrying *p*-methoxy (**4**), *p,p'*-dimethoxy (**5**), *p*-bromo (**6**), *p*-cyano (**7**), *m*-chloro (**8**), *m,m'*-dibromo (**9**), *p,p'*-dichloro (**10**), and *p,p'*-bis[(3-hydroxypropyl)oxy] (**11**) substituents have been scrutinized. Only **4** and **5** gave strong quintet and higher multiplet signals. Weak quintet signals were accompanied by strong triplet signals in **6–9**. The irradiated **10** and **11** showed only isolated triplet signals. See also: (a) Murai, H.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1980**, *102*, 5104. (b) Murai, H.; Torres, M.; Strausz, O. P. *Ibid.* **1980**, *102*, 7391.

(4) Long-chain alkyl groups are known to have a tendency to line up side by side in crystals and liquid crystals. A typical example is found in fatty acids, e.g., 2-methyloctadecanoic acid: (a) Abrahamsson, S. *Acta Crystallogr.* **1959**, *12*, 301; (b) *Ibid.* **1959**, *12*, 304.

(5) Long alkyl chains have been introduced into organic donors in order to enhance their physicochemical properties in liquid crystal phases. (a) Mueller-Westerhoff, U. T.; Nazzari, A.; Cox, R. J.; Girouard, A. M. *J. Chem. Soc., Chem. Commun.* **1980**, 497. (b) Babeau, A.; Tinh, N. H.; Gasparoux, H.; Polycarpe, C.; Torrelles, E.; Giral, L. *Mol. Cryst. Liquid Cryst.* **1982**, *72*, 171. (c) Piechocki, C.; Simon, J.; Skoulios, A.; Guillon, D.; Weber, P. *J. Am. Chem. Soc.* **1982**, *104*, 5245. (d) Inokuchi, H.; Saito, G., private communication.

(12) Buchta, E.; Andr e, F. *Chem. Ber.* **1959**, *92*, 3111.

(13) The diene **10** was formed in 89% yield, from the alcohol **8**, as a mixture of isomers containing 80% of the *E,E* isomer. The *E,E*-dihydroxy ester **16** was obtained free from other isomers by a single recrystallization. ¹H NMR (300 MHz, CDCl₃) 0.97 (d, *J* = 7.0 Hz, 3 H), 1.02 (d, *J* = 6.8 Hz, 3 H), 1.82–1.94 (m, 3 H), 2.42 (m, 1 H), 3.61 (d of d, *J* = 2.7, 8.5 Hz, 1 H), 3.68–3.80 (m, 2 H), 3.74 (s, 3 H), 5.84 (d, *J* = 15.4 Hz, 1 H), 6.08 (d of d, *J* = 8.6, 15.3 Hz, 1 H), 6.28 (d of d, *J* = 10.8, 15.3 Hz, 1 H), 7.27 (d of d, *J* = 10.8, 15.4 Hz, 1 H).

(14) Part of the projected Ph.D. Thesis of J. Zimmermann, ETH-Z rich.

(15) Hanessian, S.; Staub, A. P. A. *Tetrahedron Lett.* **1973**, 3555.

(16) ¹H NMR (300 MHz, CDCl₃) 1.10 (d, *J* = 6.7 Hz, 6 H), 1.19 (d, *J* = 7.0 Hz, 6 H), 2.52 (d of d of q, *J* = 9.5, 10.3, 6.7 Hz, 2 H), 2.71 (d of q, *J* = 2.5, 7.0 Hz, 2 H), 5.39 (d of d, *J* = 2.5, 10.3 Hz, 2 H), 5.57 (d, *J* = 15.4 Hz, 2 H), 5.65 (d of d, *J* = 9.5, 15.0 Hz, 2 H), 6.05 (d of d, *J* = 11.2, 15.0 Hz, 2 H), 6.96 (d of d, *J* = 11.2, 15.4 Hz, 2 H), 9.67 (s, 2 H).

(17) Sutter, M. A. Ph.D. Thesis, No. 7659, ETH-Z rich, 1984.

(18) In a related example the "Cram product" was also observed in a system in which chelation control would have been possible: Collum, D. B.; McDonald, J. H., III; Still, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2120.

(19) ¹H NMR (300 MHz, CDCl₃) 0.87 (t, *J* = 7.6 Hz, 3 H), 0.92 (t, *J* = 7.6 Hz, 3 H), 1.11 (t of t, *J* = 10.2, 3.9 Hz, 1 H), 1.21 (d, *J* = 6.3 Hz, 3 H), 1.31 (d of d, *J* = 12.5, 11.0 Hz, 1 H), 1.34–1.41 (br, 1 H), 1.47 (d of q, *J* = 14.4, 7.5 Hz, 1 H), 1.50–1.70 (m, 2 H), 1.77 (d of q, *J* = 14.3, 7.6 Hz, 1 H), 2.14 (d of d, *J* = 12.4, 4.9 Hz, 1 H), 3.11 (s, 3 H), 3.52 (d of q, *J* = 6.3, 10.2 Hz, 1 H), 3.90 (d of t, *J* = 4.8, 10.5 Hz, 1 H). The signal at 3.90 is due to H-4, which must be axial; for two large coupling constants to be observed.

(20) Inoue, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 174. Masamune, S.; Choy, W.; Kerdesky, F. A. J.; Imperiali, B. *J. Am. Chem. Soc.* **1981**, *103*, 1566. Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 3099.

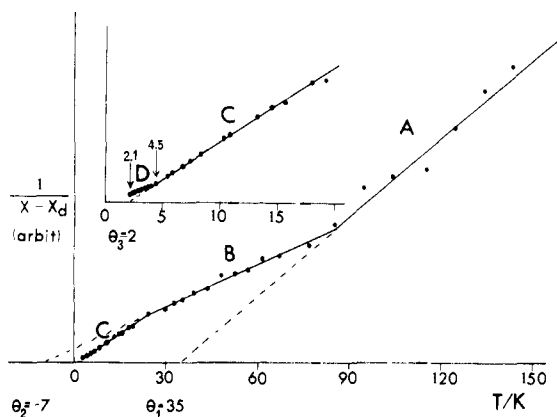


Figure 1. Temperature dependence of the reciprocal paramagnetic susceptibility for carbene species generated in polycrystalline **1**. Inset: The plot at lower temperatures than 20 K is shown on an expanded scale.

in the range 260–380 mT, accompanied by weak quintet signals at 245.8 and 258 mT. In order to examine the average spin multiplicity and temperature dependence of the magnetization of bis[*p*-(octyloxy)phenyl]carbene (**2**), the magnetic susceptibility was measured by means of a Faraday-type magnetic balance system. Magnetization of the sample obtained by photolyzing crystals of **1** at 4 K was recorded at various temperatures under the field gradient of 5 T/m generated by auxiliary coils and the main coil of 0.5 T. A $1/(\chi - \chi_d)$ vs. T plot is approximated by a set of four straight lines with three break points at 84, 23, and 4 K (see Figure 1), indicating how the magnetic interaction develops among carbene species with magnetic and/or structural transitions on lowering temperatures.⁶ The line in region A is extrapolated to give a positive Weiss temperature of 35 K. The carbene molecules are considered to be in a ferromagnetic molecular field in this region. The slope of the line decreases at temperatures lower than 80 K, showing an increase of the apparent spin multiplicity.⁷ After it passes through region B with small antiferromagnetic molecular field ($\theta = -7$ K), the region C shows a ferromagnetic molecular field again ($\theta = 2$ K), resulting in an increase of spin multiplicity at temperatures lower than 4 K (region D). The average spin multiplicity was determined by the field dependence of magnetization (M) as a function of an external main field (H) at 2.1 and 4.5 K, and magnetization curves were analyzed in terms of the Brillouin function.² The magnetization behaviors at the two temperatures were found not to be the same, and the saturation behavior at 4.5 K fits closely to that of $S = 4/2$, and that at 2.1 K is rather closer to $S = 8/2$ especially at the low H/T range. The results indicate that intermolecular magnetic interaction develops over a wider range at 2.1 than at 4.5 K, connecting four carbene molecules magnetically on the average.

In order to understand the magnetic interaction of the carbene species on the basis of their spacial arrangement in the crystals, an X-ray diffraction analysis was carried out on *p,p*-bis(octyloxy)benzophenone (**3**), at room temperature, as a model for diazo compound **1** and for the resulting carbene **2** in the crystals.⁸ The benzophenone crystallizes in the orthorhombic system and the unit cell dimensions are $a = 56.60$ (2) Å, $b = 7.395$ (2) Å, and $c = 6.332$ (2) Å, with a space group of $Pnca$; R value is 9.3% for 1616 independent reflections. The projections along a and b axes are depicted in Figure 2, showing the multilayered structure of the benzophenone units. Each layer is separated by the all-trans octyl

(6) The complex behavior in the $1/\chi_p$ vs. T plot could be rationalized by an orientational transition such as the change in the dihedral angle between two spin-distributed benzene rings of a carbene molecule.

(7) Effective paramagnetic species in this temperature range (80–150 K) is found by ESR spectroscopy to be a quintet species. The higher multiplet signals due to magnetic interaction among quintet species were observed to start at lower temperatures than 80 K.

(8) It was difficult to obtain a good crystal of **1** suitable for single-crystal analysis. An X-ray analysis on a thin crystal of the diazo compound **1** is under way. The crystals are orthorhombic and the unit cell dimensions are $a = 52.8$ Å, $b = 7.32$ Å, and $c = 7.05$ Å, with a space group of $Pnca$. Therefore the packing arrangement of **1** is supposed to be practically the same.

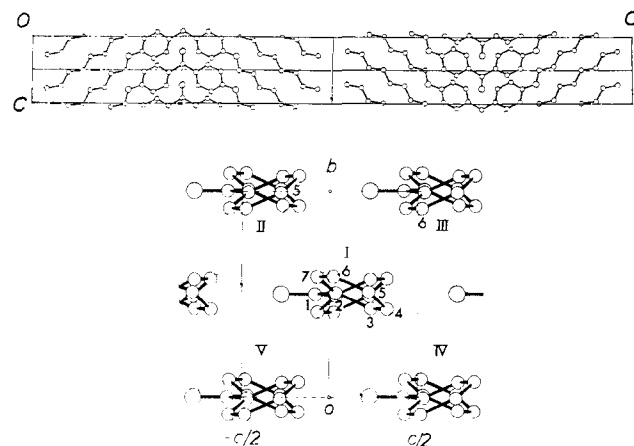


Figure 2. Crystal structure of **3** viewed along the b axis (top) and partial packing arrangement (chains and hydrogen atoms are omitted) viewed along the a axis (bottom).

chains which are aligned parallel to each other. One of the benzene rings in molecule **1** has four nearest neighbors (II–V), presenting a two-dimensional network with interactions satisfying McConnell's ferromagnetic condition.⁹ Thus if the molecules of **2** stack similarly in the crystals, ferromagnetic interaction would develop within the layer, which can be regarded as a domain in ferromagnets. Since magnetic interaction between the layers is insulated by long alkyl chains, the gross magnetic moment of the layers would align to the same direction under strong external field. If the magnetic anisotropy of the assembly of **2** within a layer is large enough, the sample may show macroscopic ferromagnetism.

Better overlap of spin-containing benzene rings and some additional force to support crystal structures should increase the magnetic interaction and would lead to organic ferromagnets. Investigation along this line is in progress in these laboratories.

(9) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910. There are several important interactions among spin-containing benzene rings. When viewed along a axis, ferromagnetic interaction prevails among benzene rings II, II', and III' in front (e.g., between C6 of II' and C5 of III', and between C5 of II' and C6 of III' with an intermolecular distance of 3.55 Å) and among benzene rings IV and IV' or V and V' in the rear.

Detection of the Static 1,2-Dimethyl-2-norbornyl Cation by Variable-Temperature ¹³C CPMAS NMR

Philip C. Myhre* and Kevin L. McLaren

Department of Chemistry, Harvey Mudd College
Claremont, California 91711

Costantino S. Yannoni*

IBM Research Laboratory, San Jose, California 95193

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NMR studies of the 2-norbornyl cation show that the positive charge is equally distributed between C1 and C2 at temperatures as low as 5 K.¹ This result allows one to restrict the barrier for a hypothetical Wagner–Meerwein shift in the 2-norbornyl cation to about 0.2 kcal mol⁻¹, if tunneling by carbon is not important.^{1,2} Carbon tunneling has been invoked in order to account for differences between the calculated and observed rate of the automerization of cyclobutadiene.³ More detailed calculations indicate

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