Liquid Crystals. 1. β-Oxygen Effect on Stabilization of Hexakis(acyloxy)benzene Mesophase

Iwao Tabushi,† Kazuo Yamamura,* and Yukihiro Okada

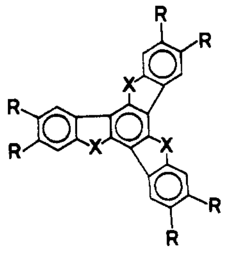
Department of Synthetic Chemistry, Kyoto University, Sakyo-ku Kyoto, 606 Japan

Received October 21, 1986

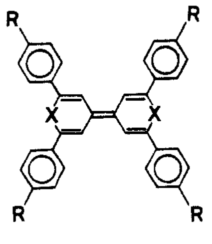
A new family of liquid crystalline (discotic) hexaesters, hexakis[(n-oxaoctanoyl)oxy]benzene ($4{\cdot}O^n$, $2 \le n \le 7$), hexakis[(3-thiaoctanoyl)oxy]benzene ($4{\cdot}S^3$), or hexakis[(2-methoxyoctanoyl)oxy]benzene (5), was prepared from hexahydroxybenzene (3) and the corresponding acyl chlorides. Satisfactory yields (14–87%) were obtained only when a gentle stream of Ar(P_2O_5–MnO treated) was introduced into the neat reaction mixture, optionally by applying a vacuum (100–200 mmHg) or by adding a base and/or hydrocarbon in order to suppress any undesired side reactions. Among the heteroatoms investigated, oxygen atom was the most effective to depress the melting point ($T_{C\text{-}M}$) from 79.8 °C for parent 4 to 16–68 °C for $4{\cdot}O^n$ ($3 \le n \le 7$), strongly indicating that incorporation of an oxygen atom into the side chain enhanced the mesophase stability of 4 relative to the crystal phase. Moreover, the mesophasic temperature ranges ($\Delta T = T_{M\text{-}I} - T_{C\text{-}M}$) for $4{\cdot}O^3$ and $4{\cdot}O^7$ were 26° and 9°, wider than ΔT = 3.6° for the parent hydrocarbon compound (4). Thus an oxygen atom suitably introduced in the side chain expanded mesophase temperature range considerably. However, no clear mesophase was observed for $4{\cdot}O^2$ or 5 but only a glass transition was observed at −75 °C or −145 °C, respectively, indicating that the introduction of an O atom at an inappropriate position such as carbonate oxygen ($4{\cdot}O^2$) or β-oxygen atom in the branched OMe (5) only breaks up the molecular order of mesophasic 4.

The relationship between structure and mesomorphic properties of a liquid crystal is important for the elucidation of molecular factors that determine mesomorphic supramolecular assembly.[1,2] For this purpose, heteroatoms have been repeatedly investigated as the constituent element other than C atom in liquid crystalline molecules.[3,4] The oxygen effect is noteworthy, because the aryl–O–R structure unit is seen in many liquid crystals and this oxygen stabilizes nematic phases, for example, in ($=NC_6H_4$-p-$OR)_2$[3a] (R = C_3H_7 to $C_{10}H_{21}$) or p-$ROC_6H_4C_6H_4$-p-CN (R = C_3H_7 to C_8H_{17}).[3b] However, destruction of the mesophase is also reported for the O atom located in a middle position of the tail in aryl $(CH_2)_nOR$ or aryl–O–CH_2–O–R_5[4] suggesting the need of further studies on the structure–mesophase stability relationship.

As to discotic liquid crystals, very limited examples of heteroatom effect are described,[5] e.g., for an O or S atom located in the core positions of truxene (1) and 2,2′,6,6′-tetrakis(p-alkylphenyl)pyran-4-ylidene (2).[5a-c] The clearing point was depressed by the structural change from the C atom to the heteroatom (O, S).



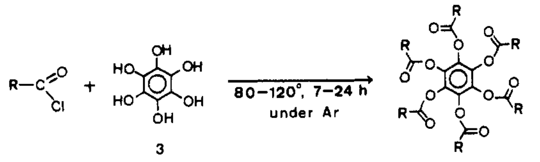
1 X = CH_2, O, S



2 X = O, S

Now we report a new family of liquid crystalline compounds, hexakis[(oxaalkanoyl)oxy]benzenes, among which hexakis[(3-oxaoctanoyl)oxy]benzene, $4{\cdot}O^3$ (Scheme I) is of special interest in exhibiting the mesophase over a very large temperature range of 26°, from 68 °C ($T_{C\text{-}M}$) to 94 °C ($T_{M\text{-}I}$). It contrasts to the rather narrow temperature range of 3.6°, from 79.8 °C to 83.4 °C, for the corresponding octanoate 4 bearing no O atom, the first member of the family.

Scheme I



4	:	$R = -\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_2\overset{7}{C}H_2CH_3$
$4 \cdot O^n$	: n=2	$-\overset{2}{O}-C_6H_{13}$
	3	$-CH_2-\overset{3}{O}-C_5H_{11}$
	4	$-C_2H_4-\overset{4}{O}-C_4H_9$
	5	$-C_3H_6-\overset{5}{O}-C_3H_7$
	7	$-C_5H_{10}-\overset{7}{O}-CH_3$
$4 \cdot S^n$	: n=3	$-CH_2-\overset{3}{S}-C_5H_{11}$
5	:	$-\underset{OCH_3}{CH}-C_6H_{13}$
6	:	$-CH_2-O-C_3H_7$
7	:	$-CH_2-O-C_7H_{15}$

Results and Discussion

The present hexaester family, $4{\cdot}O^n$ ($2 \le n \le 7$), $4{\cdot}S^3$, and 5, were prepared from hexahydroxybenzene (3) and the corresponding acyl chloride (Scheme I). In preparations

---

† Deceased March 22, 1987.

(1) Gray, G. W. *Molecular Structure and the Properties of Liquid Crystals*; Academic Press: London, 1962.

(2) (a) Chandrasekhar, S.; Sodashiva, B. K.; Suresh, K. A. *Pramana* **1977**, *9*, 471. (b) Destrade, C.; Mondon-Bernaud, M. C.; Tinh, N. H. *Mol. Cryst. Liq. Cryst. Lett.* **1979**, *49*, L-169. (c) Fugnitto, R. *J. Chem. Soc., Chem. Commun.* **1980**, 271. (d) Simon, J. *J. Am. Chem. Soc.* **1982**, *104*, 5254. (e) Tinh, N. H.; Foucher, P.; Destrade, C. *Mol. Cryst. Liq. Cryst.* **1984**, *111*, 277. (f) Chandrasekhar, S,; Sadashiva, B. K.; Suresh, K. A.; Madhusudana, N. V.; Kumar, S.; Shashidhar, R.; Venkatesh, G. *J. Phys. (Paris)* **1979**, *40*, C3-120.

(3) (a) Luckhurst, G. R.; Gray, G. W. *The Molecular Physics of Liquid Crystals*; Academic Press: London 1979; Chapter 1. (b) Gray, G. W.; Harrison, K. J.; Nash, J. A.; Constant, J.; Hulme, D. S.; Kirton, J.; Raynes, E. P. *Liq. Cryst. Ord. Fl.* **1974**, *2*, 617.

(4) (a) Kitamura, T.; Mukoh, A. *Mol. Cryst. Liq. Cryst.* **1984**, *108*, 333. (b) Weygand, C. *J. Prakt. Chem.* **1941**, *158*, 266.

(5) (a) Tinh, N. H.; Foucher, P.; Destrade, C. *Mol. Cryst. Liq. Cryst.* **1984**, *111*, 277. (b) Destrade, C.; Tinh, N. H.; Mamlok, L.; Malthete, J. *Ibid.* **1984**, *114*, 139. (c) Tinh, N. H.; Cayuela, R.; Destrade, C. *Ibid.* **1985**, *12*, 141. (d) Praefcke, K.; Poules, W.; Scheuble, B.; Poupko, R.; Luz, Z. *Z. Naturforsch.* **1984**, *39b*, 950. (e) Lehn, J.-M.; Malthete, J.; Levelut, A.-M. *J. Chem. Soc., Chem. Commun.* **1985**, 1794.

0022-3263/87/1952-2502$01.50/0

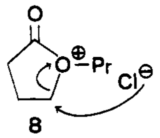
Table I. Phase-Transition Temperatures (in degrees)

compd	R		T_{C-M}	T_{M-I}	ref
4	C_7H_{15}		79.8	83.4	*a*
4·O^2	OC_6H_{13}	liquid (25 °C),	$T_g = -75$		*b*
4·O^3	$CH_2OC_5H_{11}$		68	94	*b*
4·O^4	$C_2H_4OC_4H_9$		30	32	*b*
4·O^5	$C_3H_6OC_3H_7$		43	44	*b*
4·O^7	$C_5H_{10}OCH_3$		16	25	*b*
4·S^3	$CH_2SC_5H_{11}$		66	67	*b*
5	$CH(OCH_3)CHC_6H_{13}$	liquid (25 °C),	$T_g = -145$		*b*
6	$CH_2OC_3H_7$		110	111.5	*b*
7	$CH_2OC_7H_{15}$		74	94	*b*

[a] Reference 2f. [b] Present results, purity was over 99% based on HPLC analysis.

of 4·O^n ($n = 2, 3, 4, 7$) and 4·S^3, satisfactory yields were obtained (14–87%, 110–120 °C, 7–12 h, no solvent used) only when a gently Ar stream (optionally evacuated at 100–200 mmHg) was applied to remove HCl generated very effectively from the reaction mixture. Under the reaction conditions of 100–120 °C, 5–10 h, and no Ar bubbling, which was appropriate for the preparation of 4, yields of 4·O^n were unsatisfactorily poor, ca. 0–9% and were not improved appreciably by the use of base (pyridine, anhydrous K_2CO_3 etc.).

Even under the conditions of Ar stream, the treatment of 3 with 5-oxaoctanoyl chloride at 120 °C for 2 h did not give the hexaester 4·O^5. The transformation of acyl chloride to Cl $(CH_2)_3CO_2C_3H_7$ took place readily,[6] probably via a favored cyclic transition state like 8 in a polar medium. Therefore, a nonpolar solvent, decalin, was used in this particular case to retard the chloro ester formation, affording 4·O^5 successfully in 23% yield.



8

For the preparation of 5, decalin and pyridine were used to improve the yield (15%). Without these addenda, the yield was poor (less than 3%) because of a facile elimination reaction of 2-methoxyoctanoyl chloride, since an olefinic byproduct was obtained judging from the $\nu_{C=C}$ of 1640 cm^{-1} and the NMR absorptions centered at ca. δ 5.7 observed for the reaction mixture.

Structure determinations of the desired products were made by IR (see Experimental Section) and ^{1}H NMR. Purities of the product esters were confirmed by HPLC analyses (see footnote in Table I). In DSC thermal analyses,[7] consecutive scanning (heating–cooling cycle) was carried out on each sample to certify good reproducibility. Figure 1a,b depict the DSC traces of hexakis[(3-oxaoctanoyl)oxy]benzene (4·O^3), as a typical example. As is apparent in Figure 1a,b, three-phase transitions at 48 °C, 68 °C, and 94 °C were observed on the first heating (Figure 1a). The lowest temperature transition at 48 °C was irreversible, strongly suggesting the solid–solid transition and/or the supercooling of the mesophase.[8] Two new transitions at 47 °C and 57 °C that appeared on the second heating (Figure 1b) were reproducible in the following scannings.

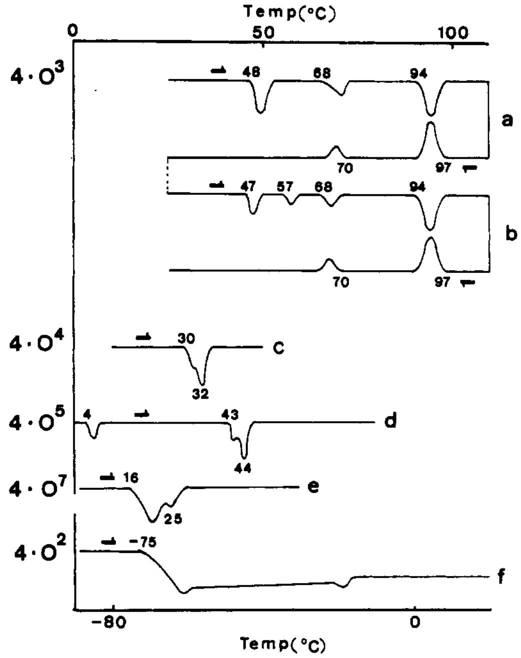


Figure 1. DSC traces for 4·O^n: (a) first heating/cooling of 4·O^3; (b) second heating/cooling of 4·O^3; (c) 4·O^4; (d) 4·O^5; (e) 4·O_7; (f) 4·O^2. Heating rate: 3°/min (a, b), 1°/min (c, d), 2°/min (e), 5°/min (f).

Table II. Transition Enthalpies and Entropies of New Mesogens 4•O^n and 5–7

	melting point		clearing point	
compd	ΔH, kcal/mol	ΔS, eu	ΔH, kcal/mol	ΔS, eu
4[a]	10.7	30	4.5	13
4·O^2				*b*
4·O^3	0.3	0.9	1.0	2.7
4·O^4	1.9	6.3	2.5	8.2
4·O^5	1.0	3.2	1.9	6.0
4·O^7	1.6	5.5	0.4	1.3
4·S^3	4.4	13	4.5	13
5				*b*
6	3.0	7.8	2.4	6.2
7	0.6	1.8	0.7	2.0

[a] Reference 2f. [b] Glass transition.

The higher temperature transitions, T_{C-M} = 68 °C and T_{M-I} = 94 °C, were reproducible. In the 68–94 °C temperature range, 4·O^3 showed a turbid viscous mesophasic state, where a birefringent texture was also observed by polarizing microscopy. The texture of 4·O^3 under the microscope was assigned as broken-fan based on a comparison with the textures reported for the parent discotics.[2a] These observations strongly support 4·O^3 as a mesomorphic compound in the 68–94 °C temperature range. More important, however, is the fact that T_{M-I} of 94 °C for 4·O^3 is higher than T_{M-I} of 83.4 °C for the parent hydrocarbon ester, 4, since this means that the β O atom has stabilized the mesophase relative to the isotropic phase to a considerable extent. Below 68 °C (T_{C-M}) 4·O^3 was solid, and the transitions seen at 47 °C and 57 °C are most probably the solid–solid transitions.[8]

Other oxa homologs 4·O^n (n = 4, 5, 7) also showed liquid crystalline phases and their DSC traces are shown in Figure 1. The textures of 4·O^4, 4·O^5, and 4·O^7 under the polarizing microscope were broken-fan,[2a] fan-and-flower like particle,[2b] and fan,[2b] respectively. The observed crystal–mesophase transition temperature (melting point, T_{C-M}) and mesophase–isotropic phase transition temperature (clearing point, T_{M-I}) are summarized in Table I. The transition enthalpy and transition entropy are given in Table II. As is apparent in Table I, T_{C-M} and T_{M-I} are

---

(6) A similar transformation is reported for $C_2H_5O(CH_2)_3COCl$ to rearrange to $Cl(CH_2)_3CO_2C_2H_5$ in $SOCl_2$; Blicke, F. F.; Wright, W. B.; Zienty, M. F. *J. Am. Chem. Soc.* **1941**, *63*, 2488.

(7) McAdie, H. G. *Thermal Analysis*; Schwenker, R. F., Jr.; Garn, P. D., Ed.; Academic Press: London, 1969, Vol. I.

(8) Sorai, M.; Tsuji, K.; Suga, H.; Seki, S. *Mol. Cryst. Liq. Cryst.* **1980**, *80*, 33.

highly dependent on the location of the O atom in the present seven-membered chains. T_{C-M} was lowered markedly from 79.8 °C for parent 4 to −145 to +68 °C for the present heteroatom-containing compounds (see Table I). Moreover, oxy compounds $4{\cdot}O^3$ and $4{\cdot}O^7$, respectively, showed the mesophase temperature ranges 26° and 9°, considerably wider than 3.6° for the parent hydrocarbon compound 4. These observations strongly suggest that the oxygen atom suitably introduced in the alkyl tail enhanced the thermal stability of the mesophase relative to the crystal phase.[9]

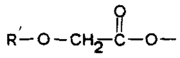
Further evidences for the mesomorphic properties of $4{\cdot}O^4$ were obtained from the X-ray diffraction pattern of the birefringent viscous mesophase. For example, a main characteristic seen for $4{\cdot}O^4$ was a very broad diffraction with a maximum of intensity corresponding to $d = \lambda/(2 \sin \theta) = 4.4$ Å. Such a diffuse diffraction is probably due to the disordered interdisk distance, revealing the structural similarity to hexakis[p-(*n*-dodecyloxy)benzoyl]cyclam[5e] and 2,3,6,7,10,11-hexakis[(3-oxaalkanoyl)oxy]triphenylene,[12] both of which show similar diffuse diffractions centered at $d = 4.5$ Å due to the disorder of their interdisk distances. Rather sharp diffractions were also observed at $d = 21.8$, 12.9, and 11.0 Å for $4{\cdot}O^4$. These were reasonably assigned to d_{100}, d_{110}, d_{200} spacings, the evaluated lattice constant, $a = 25$ Å, being very close to the molecular diameter.[2a]. These observations are consistent with a hexagonal columnar organization.

Hexakis[(3-thiaoctanoyl)oxy]benzene ($4{\cdot}S^3$), a sulfur analogue of $4{\cdot}O^3$, exhibited T_{C-M} of 66 °C, indicating that the β S atom effectively stabilized the mesophase compared with the crystal phase. However, its T_{M-I} of 67 °C was lower than that of $4{\cdot}O^3$ by 27° (Table I). The introduction of an O atom as a MeO pendent substituent on the side arm to give hexakis[(2-methoxyoctanoyl)oxy]benzene (5) was carried out via Scheme I. The MeO derivative 5 exhibited no clear mesophase (Table I).

Carbonate $4{\cdot}O^2$ in which an oxygen atom was incorporated at the C_2 position was also prepared. $4{\cdot}O^2$ is liquid at room temperature, and no mesophase was found at lower temperatures down to −80 °C, although a glass transition appeared at ca. −75 to −15 °C upon heating as the DSC trace shows (Figure 1f).

In order to study the present noticeable β-oxygen effect (see $4{\cdot}O^3$) in more detail, we have prepared 6 and 7, which carry similar β-oxygens in the chains of different length, (3-oxahexanoyl)oxy and (3-oxadecanolyl)oxy, respectively (Scheme I). An extremely narrow ΔT = ca. 1.5° for hexakis[(3-oxahexanoyl)oxy]benzene (6) was observed, although 7 exhibited only a slightly narrower $\Delta T = 20°$ than 26° for $4{\cdot}O^3$ (see Table I). These observations strongly indicate that an appropriate chain length is also important.

In conclusion, the oxygen atoms and the sulfur atom located in the alkyl tails of 4 stabilized the mesophase compared with the crystal phase (depressing of the melting point, T_{C-M}). Among these, the β-oxygen atom of the (3-oxaacyl)oxy (9) type was particularly noticeable, since



$R'{-}O{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}$

9

it gave the widest mesophasic temperature ranges (ΔT) of 1.5–26°. More important was the raising of the clearing point by the β-oxygen atom as seen for $4{\cdot}O^3$, 6, and 7. As far as the magnitude of ΔT is concerned, the (3-oxaoctanoyl)oxy tail ($R' = C_5H_{11}$) was superior to (3-oxahexanoyl)oxy ($R' = C_3H_7$) or (3-oxadecanoyl)oxy ($R' = C_7H_{15}$). The present oxygen effect, especially the β-oxygen effect, may provide a new promising means for the "tail design" which will be applicable to the preparations of new discotic liquid crystalline compounds.

Experimental Section

General. ^1H NMR spectra were obtained with a JEOL JNM PMX 60 SI NMR spectrometer. ^{13}C NMR spectra were measured with a JEOL JNM FX90Q FT NMR spectrometer. IR spectra were recorded on a Hitachi Model 260-50 spectrophotometer. A Nippon Kogaku POH microscope was used for the polarizing microscopy.

X-ray diffraction data were collected on a Rigaku X-ray diffractometer RAD-IIA by Nihon Kogyo Company. Sample purity was determined by HPLC on a Waters SiO_2 radial pak column (8 mm × 100 mm) by using a Shimadzu SPD-6AV UV–vis spectrophotometric detector. Microanalyses were performed at the Microanalytical Center of Kyoto University.

Materials. Hexahydroxybenzene (3) was prepared according to the reported procedure.[10] Manganese oxide, MnO, was freshly prepared by pyrolysis of manganese oxalate at 350 °C, 10^{-2} Torr as reported.[11] Dry pyridine was obtained by refluxing first on KOH and then on BaO, followed by distillation under Ar. Commercially available decalin was dried over Na and distilled.

Hexakis[(3-oxaoctanoyl)oxy]benzene ($4{\cdot}O^3$). A mixture of 0.5 g (2.9 mmol) of 3 and 5.8 g (35 mmol) of 3-oxaoctanoyl chloride was heated at 110 °C under an atmosphere of dry, deoxygenated Ar. Thus, $MnO{-}P_2O_5$-treated Ar was introduced into the reaction mixture through a glass capillary at 100 mmHg by applying vacuum during the reaction to remove HCl generated. After 12 h, the excess acyl chloride was removed by a distillation in vacuo (0.2 mmHg) to give a viscous oil, which was subjected to column chromatography on silica gel (Merck 60, 70–230 mesh, 2 cm × 30 cm) using cyclohexane (200 mL) and then benzene (600 mL) as eluent. Benzene fractions containing $4{\cdot}O^3$ were collected (total eluents, 100 mL) and the solvent was evaporated to dryness to give 1.3 g of drude $4{\cdot}O^3$. Further purification by successive recrystallizations was carried out from EtOH–H_2O (10:1, v/v), *n*-hexane–EtOH (10:1, v/v), and EtOH, giving 1.1 g (0.1 mmol, 38%) of pure $4{\cdot}O^3$ (99% on HPLC analysis). $4{\cdot}O^3$: ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 28.1, 29.0, 67.5, 72.6, 133.8, 165.4; IR ν_{max} (KBr) 1800 ($\nu_{C=O}$), 1110 (ν_{CO}) cm^{-1}. Anal. Calcd for $C_{48}H_{78}O_{18}$: C, 61.13; H, 8.34. Found: C, 61.06; H, 8.51.

Hexakis[(4-oxaoctanoyl)oxy]benzene ($4{\cdot}O^4$). $4{\cdot}O^4$ was prepared from 0.5 g (2.9 mmol) of 3 and 5.8 g (35 mmol) of 4-oxaoctanoyl chloride in a manner similar to that described for $4{\cdot}O^3$, except that the successive recrystallizations were carried out from EtOH–H_2O (10:1, v/v) and then twice from EtOH. $4{\cdot}O^4$ (1.6 g, 87%); IR ν_{max} (neat) 1780 ($\nu_{C=O}$), 1110 (ν_{CO}) cm^{-1}. Anal. Calcd for $C_{48}H_{78}O_{18}$: C, 61.13; H, 8.34. Found: C, 61.13; H, 8.50.

Hexakis[(7-oxaoctanoyl)oxy]benzene ($4{\cdot}O^7$). A 0.3-g (1.74 mmol) of 3 was treated with 3.5 g (21 mmol) of 7-oxaoctanoyl chloride at 110 °C for 7 h under Ar as described above. After the workup as described above, recrystallizations were carried out three times from EtOH at −50 °C (EtOH–dry ice). $4{\cdot}O^7$, which has a low melting point, was collected in each recrystallization by using a Buchner funnel chilled at 10 °C. $4{\cdot}O^7$ (0.23 g, 14%): IR ν_{max} (neat) 1788 ($\nu_{C=O}$), 1096 (ν_{CO}) cm^{-1}. Anal. Calcd for $C_{48}H_{78}O_{18}$: C, 61.13; H, 8.34. Found: C, 60.85; H, 8.57.

Hexakis[(5-oxaoctanoyl)oxy]benzene ($4{\cdot}O^5$). The hexaesterification reaction of 0.15 g (0.86 mmol) of 3 with 1.7 g (10 mmol) of 5-oxaoctanoyl chloride was successfully carried out at 120 °C, 12 h, only when a solvent (decalin, 5 mL) was added as described in the text. After prepurification by a column chromatography on SiO_2, successive recrystallizations were carried out from MeOH–H_2O (1:1, v/v), MeOH–EtOH–H_2O (1:1:1, v/v), and then MeOH–H_2O (10:1, v/v), affording 0.19 g (0.20 mmol, 23%) of $4{\cdot}O^5$: IR ν_{max} (neat) 1770 ($\nu_{C=O}$), 1080 (ν_{CO}) cm^{-1}. Anal. Calcd for $C_{48}H_{78}O_{18}$: C, 61.13; H, 8.34. Found: C, 61.23; H, 8.43.

Hexakis[(2-oxaoctanoyl)oxy]benzene ($4{\cdot}O^2$). 3 (0.3 g, 1.74 mmol) and 2-oxaoctanoyl chloride (3.5 g, 21 mmol) were heated

---

[9] de Jeu, W. H. *J.* Phys. (*Paris*) **1977**, *38*, 1265.

[10] Fatiadi, A. J.; Sager, W. F. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, p 595.

[11] Jampolsky, L. M.; Kaiser, M. B.; Sternbach, L. H.; Goldberg, M. W. *J. Am. Chem. Soc.* **1952**, *74*, 5222.

[12] Tabushi, I.; Yamamura, K.; Okada, Y., to be published.

at 120 °C, 8 h. Purification was carried out by successive SiO_2 column chromatographies—the first chromatography by eluting with cyclohexane, benzene, AcOEt, and then EtOH, successively, and the second chromatography by eluting with cyclohexane, benzene, and then AcOEt, successively—affording 0.35 g (0.38 mmol, 22%) of pure $4{\cdot}O^2$: IR ν_{max} (neat) 1780 ($\nu_{C=O}$), 1210 (ν_{CO}) cm^{-1}. Anal. Calcd for $C_{48}H_{78}O_{18}$: C, 61.13; H, 8.34. Found: C, 61.42; H, 8.52.

Hexakis[(2-methoxyoctanoyl)oxy]benzene (5). 3 (0.15 g, 0.86 mmol) and 2-methoxyoctanoyl chloride (2.0 g, 10 mmol) in the presence of dry pyridine (0.5 g, 6.3 mmol) and a solvent (decalin, 5 mL) were heated at 80–105 °C, 24 h. After a chromatographic purification through a SiO_2 column, HPLC analysis indicated that the crude **5** still contained four minor impurities, which were not easily eliminated by attempts of recrystallizations. Therefore, the final purification was performed by a preparative HPLC (SiO_2 column, CH_2Cl_2–CH_3CN = 100:3.5 (v/v), affording pure **5** (15%): IR ν_{max} (neat) 1790 ($\nu_{C=O}$) 1092 (ν_{CO}) cm^{-1}. Anal. Calcd for $C_{60}H_{102}O_{18}$: C, 64.84; H, 9.25. Found: C, 64.96; H, 9.26.

Hexakis[(3-thiaoctanoyl)oxy]benzene ($4{\cdot}S^3$) was prepared in a manner similar to that described for $4{\cdot}O^3$. $4{\cdot}S^3$: 64% yield; IR ν_{max} (KBr) 1774 ($\nu_{C=O}$) 1102 (ν_{CO}) cm^{-1}. Anal. Calcd for $C_{48}H_{78}O_{12}S_6$: C, 55.46; H, 7.56; S, 18.51. Found: C, 55.55; H, 7.62; S, 18.37.

Differential Scanning Calorimetry. DSC thermal analyses were performed with a Seiko DSC calorimeter (I&E Mode DSC-10 or DSC-20 calorimeter combined with a Seiko SSC/580 thermal controller). For the low temperature DSC measurements, a cooling accessory, Seiko 56 US-400, was employed with liquid N_2 as a coolant. Each sample (0.8–13 mg) was sealed in a Al pan with a sealer. The heating rate was 1–5°/min. The DSC scanning was made consecutively (more than twice) on each compound until good reproducibility of phase-transition temperatures (see also text) was observed. In the case of $4{\cdot}O^3$, a crystal–crystal transition appeared at 48 °C only in the first heating. In the second heating two new transitions appeared at 47 °C and 57 °C, which were reproducible and reserved in the consecutive scannings. The observed good reproducibility of the phase-transition temperatures (±1.5 °C) suggests that a degradation of compound was not appreciable at all in the presence DSC measurements. The phase-transition temperatures were not changed when the sample was sealed in the Al pan under Ar atmosphere.

Acknowledgment. This work was supported by the Japan Ministry of Education, Science and Culture, Grant-in-Aid for Specially Promoted Research No. 61065003. We thank Prof. T. Higuchi, Osaka City University, for helping with the X-ray analysis.

Supplementary Material Available: Proton NMR data for hexaesters $4{\cdot}O^{2,3,4,5,7}$, $4{\cdot}S$, and **5** (1 page). Ordering information is given on any current masthead page.

Carbon Monosulfide as Reagent in Organic Synthesis. A Mechanism Study Based on the Frontier Orbital Approach

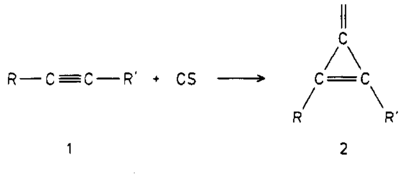
Karl Anker Jørgensen,* Ejner K. Moltzen,† and Alexander Senning

Department of Organic Chemistry, Chemical Institute, Aarhus University, DK-8000 Århus C, Denmark

Received October 20, 1986

The cycloaddition and insertion reactions of CS have been studied by using the frontier orbital approach. Calculations of the symmetry, HOMO and LUMO energies and the atomic net charge at carbon for CS lead to a comparison in reaction pattern with singlet CR_2 (carbenes). For the cycloaddition reaction it is suggested that the first step is an electrophilic attack of the vacant p orbital of the CS carbon on the π bond of the acetylene. The reactivity of CS toward acetylenes is analyzed by using electrostatic as well as frontier overlap considerations. For the insertion reactions a similar approach is used. The results obtained are discussed in relation to experiments.

Carbon monosulfide, CS, has been known for more than a century, and in spite of its unstable nature it has been the subject of numerous investigations, mainly in the spectroscopic[1] and theoretical[2] fields, but also the reactions of CS with O and O_2 have been the subject of much interest.[3] Recently CS has been introduced as a new reagent in organic synthesis as a reaction partner in cycloadditions[4] as well as α insertions.[5] The reaction of CS with acetylenic derivatives, **1**, leads to cyclopropenethiones, **2**, (eq 1). The reaction 1, however, is mainly restricted to amino- and diaminoacetylenes whereas aminothioacetylenes ($R_2NC{\equiv}CSR'$), bis(ethylthio)acetylene, di-*tert*-butoxyacetylene, bis(methylseleno)acetylene, strained acetylenes, anthracene, cyclooctatetraene, and azulene did not react with CS under the standard reaction conditions.[4,5]



(1)

1 2

---

† Present address: H. Ludbeck A/S, DK-2500 Valby, Denmark.

(1) See, e.g.: (a) Cossart, D.; Horani, M.; Rostas, J. *J. Mol. Spectrosc.* **1977**, *67*, 283. (b) Yang, S. C.; Freedman, A.; Kawasaki, M.; Bersohn, R. *J. Chem. Phys.* **1980**, *72*, 4058. (c) Saever, M.; Hudgens, J. W.; De Corpo, J. J. *J. Chem. Phys.* **1982**, *70*, 63. (d) Schofield, K. *J. Phys. Chem. Ref. Data* **1979**, *8*, 723. (e) Obase, H.; Tsuji, M.; Nishimura, U. *Chem. Phys.* **1981**, *57*, 89; **1984**, *87*, 93.

(2) See, e.g.: (a) Robbe, J. M.; Schamp, J. *J. Chem. Phys.* **1976**, *65*, 5420. (b) Cossart, D.; Bergeman, T.; *J. Chem. Phys.* **1976**, *65*, 5462. (c) Wilson, S. *J. Chem. Phys.* **1977**, *67*, 4491. (d) Green, S. *Chem. Phys.* **1978**, *31*, 425; **1979**, *40*, 1. (e) Raine, G. P.; Schaefer, H. F., III; Haddon, R. C. *J. Am. Chem. Soc.* **1983**, *105*, 194.

(3) See, e.g.: (a) Hsu, D. S. Y.; Shaub, W. M.; Burks, T. L.; Lin, M. C. *Chem. Phys.* **1979**, *44*, 143. (b) Black, G.; Jusinski, L. E.; Slanger, T. G. *Chem. Phys. Lett.* **1983**, *102*, 63. (c) Lilenfeld, H. V.; Richardson, R. J. *J. Chem. Phys.* **1977**, *67*, 3991.

(4) (a) Krebs, A.; Güntner, A.; Senning, A.; Moltzen, E. K.; Klabunde, K. J.; Kramer, M. P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 729. (b) Lütjens, H.; Moltzen, E. K.; Krebs, A.; Senning A., unpublished results. (c) Moltzen, E. K. Cand. Scient. Theses, Aarhus University, 1985.

(5) (a) Klabunde, K. J.; Kramer, M. P.; Senning, A.; Moltzen, E. K. *J. Am. Chem. Soc.* **1984**, *106*, 263. (b) Moltzen, E. K.; Senning, A.; Kramer, M. P.; Klabunde, K. J. *J. Org. Chem.* **1984**, *49*, 3854. (c) Moltzen, E. K.; Senning, A.; Kramer, M. P.; Klabunde, K. J. *J. Org. Chem.* **1987**, *52*, 1156. (d) Moltzen, E. K.; Jensen, B.; Senning, A. *Sulfur Lett.* **1986**, *4*, 203. (e) Moltzen, E. K.; Jensen, B.; Senning, A. *Acta Chem. Scand., Ser. B* **1986**, *B40*, 609.

0022-3263/87/1952-2505$01.50/0