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Structural characterization of thermotropic liquid crystalline dihydroxydicarbosilane mesophase

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Molecular mechanics (MM) calculations of the structure formed by bis(hydroxydimethylsilyl)-methane $[(CH_3)_2(HO)Si]_2CH_2$ (MDCS) molecules have been performed. The calculations lead us to conclude that MDCS can form a columnar liquid crystalline phase which consists of supramolecular H-bonded associates similar to those found earlier for siloxane compounds of the same type. Synthesis of MDCS was performed. IR, NMR, DSC and XRD (powder and single crystal) investigations have shown the existence of a LC phase in a narrow temperature range. The computational and experimental results suggest the existence of similar columnar LC phases in a wider temperature range for Et-, Pr-, and Bu-substituted bis(hydroxydialkylsilyl)methane.

1. Introduction

In our previous work it was shown that some compounds of the dihydroxydisiloxanes (DSO) series of the general formula $[R_2(HO)Si]_2O$ ($R = \text{Alk}$) [1–7], namely compounds with $R = \text{Et}$, *n*-Pr, *n*-Bu, are thermotropic liquid crystals, and they form a new class of liquid crystalline phases built of columnar H-bonded associates. One of the silanediols, $R_2Si(OH)_2$, $R = iso$-Bu, di-isobutylsilanediol forming a thermotropic mesophase [8] is also assigned to this class. There are two reasons to treat these compounds as a special group of LC compounds. First, their molecules have no anisometric form, which is common for mesogenic compounds, and second, they consist of infinite H-bonded associates that have a nearly cylindrical shape with a flexible alkyl exterior. This alkyl exterior looks very similar to the 'liquid' exterior of columns in columnar discotic mesophases [9]. The structure of H-associates in crystals of Et- and Pr-DSO is shown in scheme 1 (*a*). The crystal structure of di-isobutylsilanediol has not yet been determined; therefore we present one of the proposed structures [8], scheme 1 (*b*).

It should be mentioned that DSO with Ph, Me, and *iso*-Pr substituents also form columnar H-bonded associates in crystals as does DSO with $R = \text{Et}$ and *n*-Pr, but these associates do not form mesophases, or form mesophases in a very narrow temperature interval [2, 6, 7]. For molecules with Ph substituents this can be related to the rigidity of the substituent, and for molecules with $R = \text{Me}$ the alkyl exterior is minimal. The structures of H-bonded associates in these compounds are the same as those for Et- and *n*-Pr-substituted DSO [3, 4]. The compound with $R = iso$-Pr has the other H-bonded system (scheme 2), with an H-bond bridge between the

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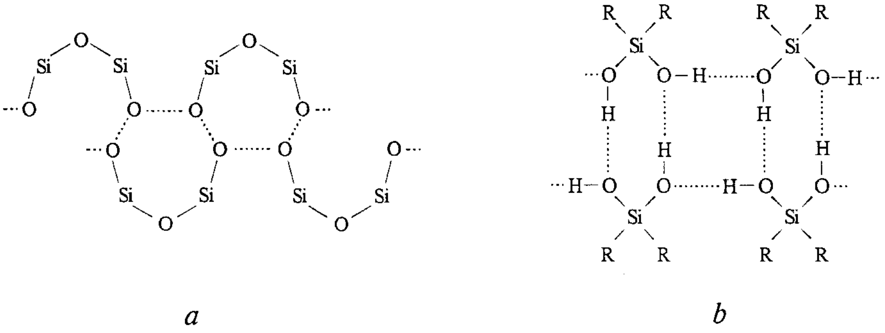
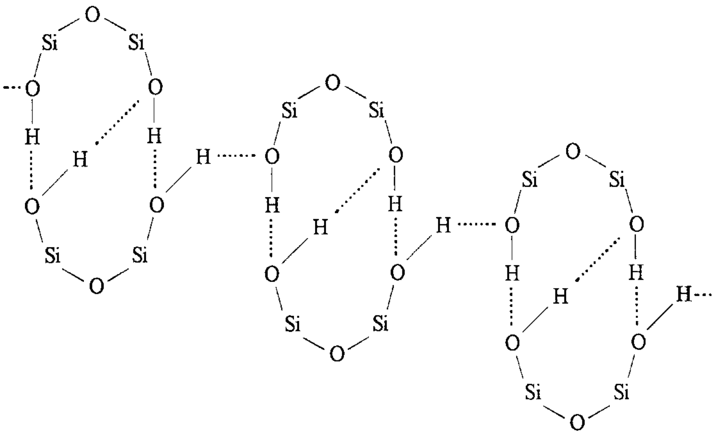


Scheme 1.

a *b*



Scheme 2.

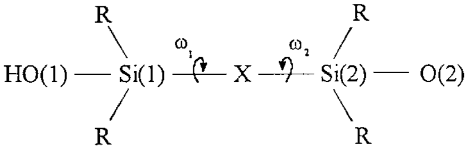
H-bonded dimer associates, which does not form a pattern with equal cooperative H-bonds, as in the crystals of other DSO compounds. Most probably this type of supramolecular organization is not stable enough on heating to form a columnar LC phase. A similar type of thermotropic columnar mesophase formed by H-bonded bisamide molecules was described recently [10].

The mesogenic properties of the above mentioned compounds gave us reason to look for analogues which can form the same or similar systems of H-bonds and therefore to form a liquid crystalline phase. Preliminary analysis of DSO analogues, bis(hydroxydimethylsilyl)-methane (MDCS) and dihydroxytetramethyldisilthianes ($[R_2(HO)Si]_2X$, $X = CH_2, S$), in order to find mutual features and differences of these compounds by the method of molecular mechanics (MM) has recently been performed [11].

In the present paper the results of MM calculations, synthesis, and characterization by NMR and IR spectroscopy, X-ray analysis and DSC of the first representative of a new chemical class of liquid crystals (MDCS) are presented.

2. Molecular mechanics' modelling of MDCS

Conformational analysis of the MDCS molecule was performed in comparison with the recently studied MDSO molecule [5]. All calculations were performed on a MicroVAX-3100 computer using the MM3 program [12], with special parameters fitted for the Si–O residue. The structure of the isolated molecules was studied as well as the structures of the H-bonded associates. The main conformational parameters determining the structure of the MDSO and MDCS isolated molecules are the torsion angles O(1)–Si(1)–X–Si(2) (ω_1) and O(2)–Si(2)–X–Si(1) (ω_2), where $X = O$, CH_2.



We mapped the conformational energy (during the calculations the angles were varied in the range 0–360° with steps of 10°). At each point for every pair of torsion angles ω_1 and ω_2 energy minimization with respect to all geometry parameters was achieved and two principal characteristics, the energy (E) and the O...O distance ($r_{O...O}$), were analysed. Functions $f(\omega_1; \omega_2)$ obtained are symmetric with respect to the diagonals of the field of variables $\omega_1[0; 360]$, $\omega_2[0; 360]$. Functions $E(\omega_1; \omega_2)$ are shown on figure 1. The distances $r_{O...O}(\omega_1; \omega_2)$ (Å) (see below) have minimum values when the torsion

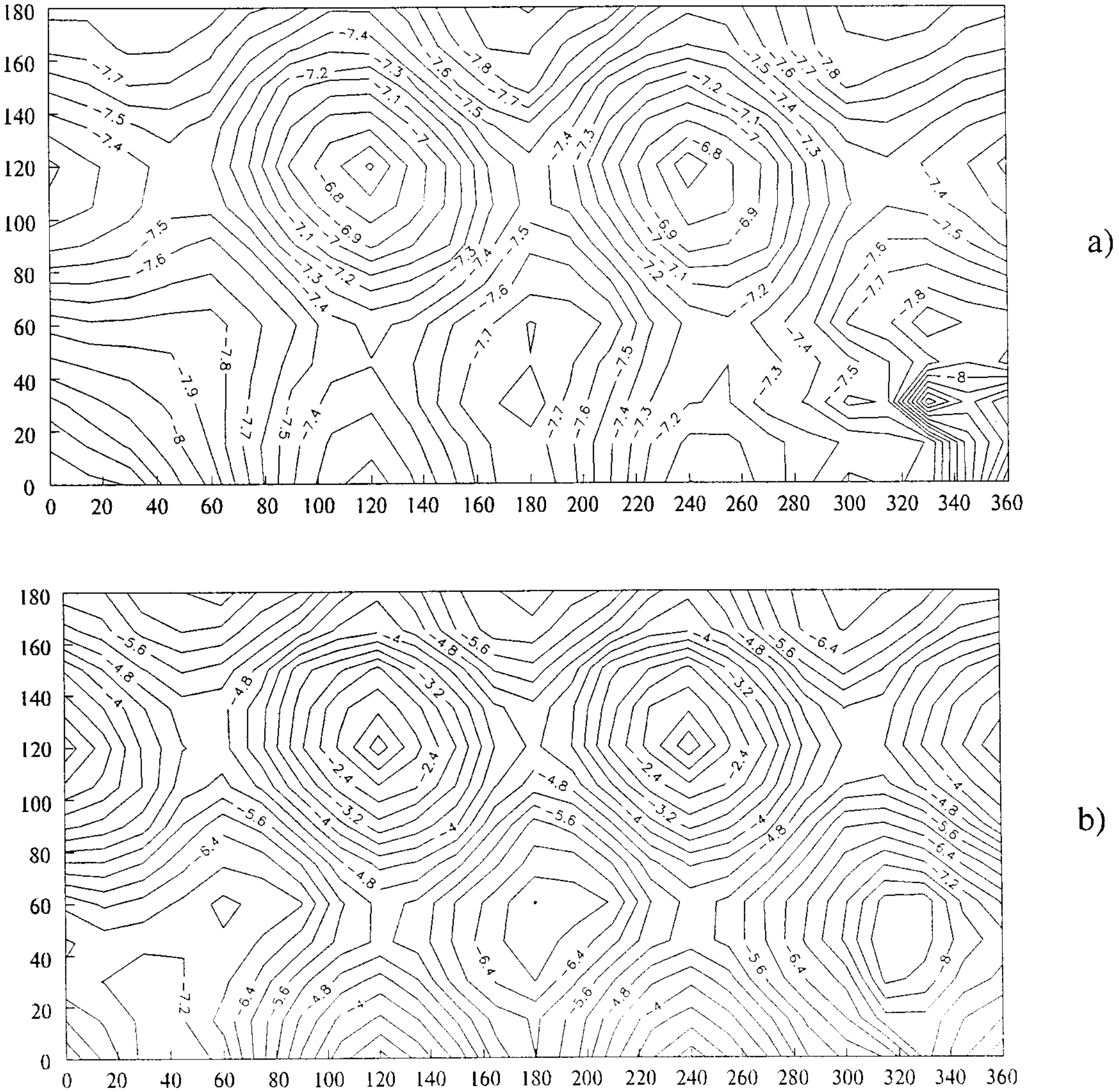
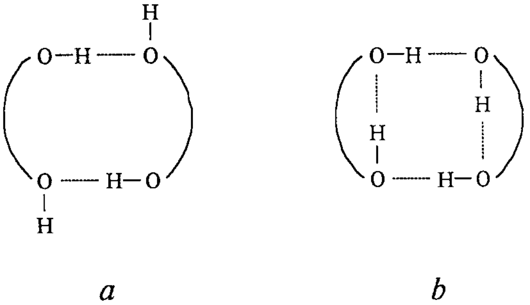


Figure 1. Conformational energy maps for MDSO (*a*) and MDCS (*b*).

angles are close to zero and have maximum values when $\omega_1 = \omega_2 = 180°$:

ω_1	ω_2	$X = O$	$X = CH_2$
0°	0°	3·059	2·870
180°	180°	5·158	5·648

H-associates investigated are shown diagrammatically in scheme 3, where the molecular skeleton is denoted by the arc HO⌒O.



Scheme 3.

Among all hypothetical H-associates, we took into consideration only H-bonded associates which resemble those found in DSO compounds. Investigation of the H-associate shown in scheme 1 (*a*), i.e. infinite H-bonded ribbons, cannot be performed by MM3 calculations with a reasonable accuracy. The structures of dimer *a* (scheme 3) for MDSO and MDCS are shown in figure 2, and the results of calculations are listed in table 1. The values of the energy of dimer *a*, where only half of the O and H atoms are involved in hydrogen bonding, include an additional energy equal to $-2\,\mathrm{kcal\,mol^{-1}}$ per hydrogen bond, which does not actually occur, but is potentially possible. This correction is required by

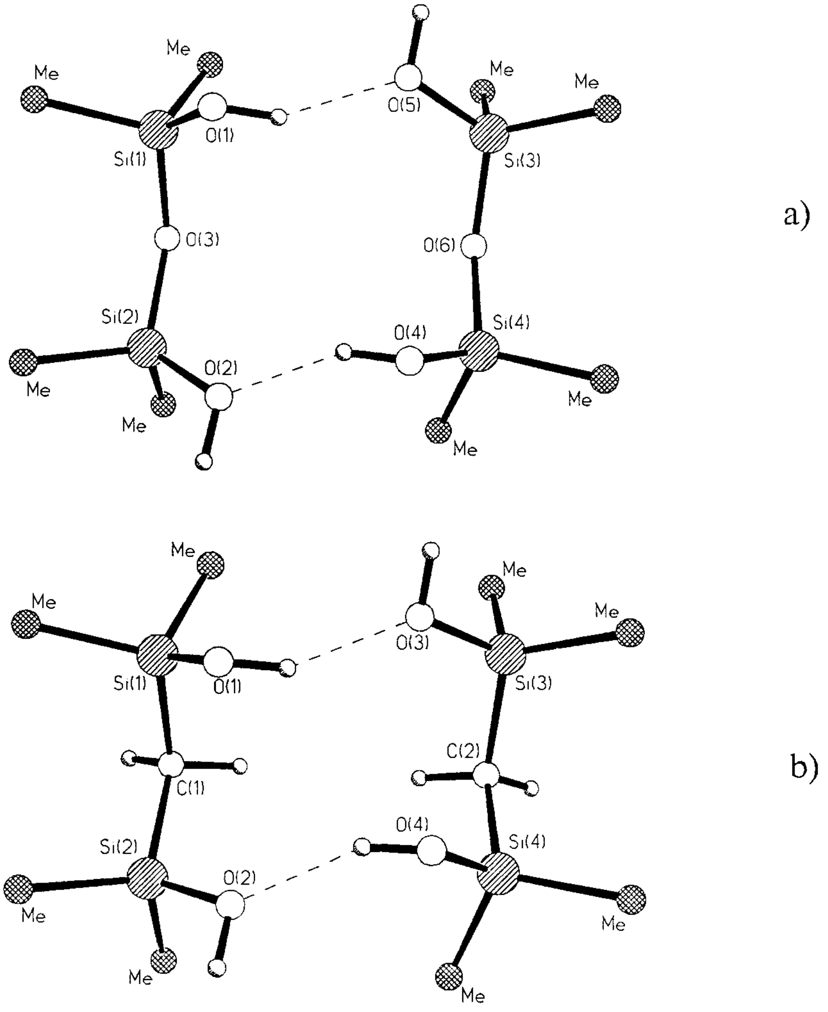


Figure 2. Dimeric H-associates of MDSO (*a*) and MDCS (*b*).

Table 1. Optimized energies per molecule of the H-associates of MDSO and MDCS.

	E/kcal mol^{-1}	
Compound	*a*	*b*
MDSO	−19·13	−18·15
MDCS	−14·74	−14·67

the assumption that in real structures these associates are linked together by hydrogen bonds. This external H-bond correction (−2 kcal mol^{-1}) is equal to an average value of the calculated energies of intermolecular hydrogen bonds for molecules of this type, which are within the range −2·1 to −1·9 kcal mol^{-1}.

3. Experimental

MDCS was prepared by the hydrolysis of bis(chlorodimethylsilyl)methane in the presence of aniline as an acceptor of HCl. Bis(chlorodimethylsilyl)methane was prepared by techniques described in [13]. The structure of MDCS, which is shown in figure 3, was confirmed by ^{1}H, and ^{29}Si NMR, and by IR. NMR spectra of MDCS in $(CD_3)_2CO + CCl_4$ solution were measured using a Bruker 200-SY spectrometer; IR spectra of MDCS as tablets with KBr, and in CCl_4 solution, were measured

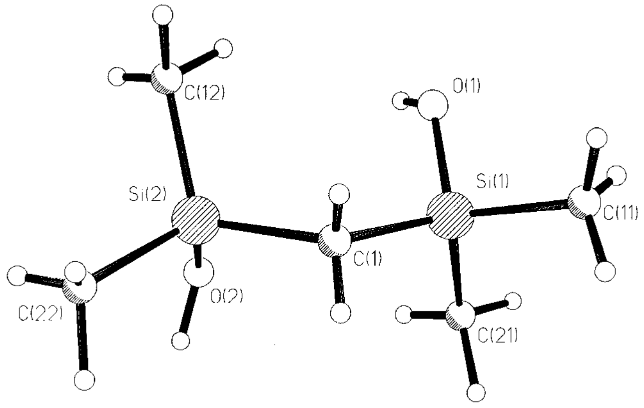


Figure 3. X-ray structure of the MDCS molecule.

using a UR-20 spectrophotometer. In ^{1}H spectra 0·084, 0·077 and 4·277 ppm signals were observed, and the correlation of integral intensity was 6 : 1 : 1, with respect to CH_3, CH_2 and OH groups. In ^{29}Si NMR spectra a 19·04 ppm singlet was observed. The IR spectra of MDCS with KBr have absorption bands at 827, 861 (Si–C), 1047 (Si–O), 1252, 1245 (Si–C), and 3200–3600 (OH) cm^{-1}; in CCl_4 solution, concentration 0·001–0·005 mol l^{-1}, wide field absorption is present (3200–3600 cm^{-1}), and a tight band at 3670 cm^{-1} at a concentration of 0·005 mol l^{-1}, with respect to the OH group.

Single crystals of MDCS were prepared by recrystallization from hexane solution as very thin needles, of unsatisfactory quality for single crystal X-ray analysis. Specimens for X-ray studies of crystal unit cell parameters were prepared by stacking about 200 needles aligned in parallel into a compact bundle (this method and its advantages, as well as the estimation of unit cell parameters, were described in detail in [14]). Temperature dependent X-ray measurements in the interval from +18 to +95°C were carried out using randomly aligned thin needles. The WAX patterns were recorded with an IRIS-3.0 instrument (CuK$_\alpha$, Ni filter, flat cassette), the diffractograms with a DRON-3M apparatus (CuK$_\alpha$, curved crystal, monochromator on the primary beam). The diffractometer was equipped with a texture attachment and with a heating chamber with automated temperature monitoring (precision ±1°C). X-ray patterns and diffractograms were registered in the transmission mode. X-ray investigations at +18°C characterize the unit cell as orthorhombic (space group $P2_12_12$; unit cell parameters are $a = 5·96$ Å, $b = 11·39$ Å, $c = 14·60$ Å; axis a corresponds to the long axis of the needles).

Single crystals of MDCS of a good quality were prepared by slow crystallization from benzene solution at 15°C. X-ray structural investigation of MDCS was carried out at −120°C on a Siemens P3/Pc diffractometer (MoK$_\alpha$ $\lambda = 0·71069$ Å, graphite monochromator, $\Theta/2\Theta$-scan, $2\Theta < 60°$). At −120°C the crystals are orthorhombic, space group $P2_12_12_1$, $Z = 4$. Unit cell parameters and other important crystallographic characteristics are: $a = 5·971(13)$ Å, $b = 11·32(3)$ Å, $c = 14·54(3)$ Å, $V = 983(4)$ Å^3, $d_{calc} = 1·110$ g cm^{-3}, $F(0\ 0\ 0) = 360$, $\mu = 0·306$ mm^{-1}. The total number of the measured reflections was 1426. The structure was solved by the direct method and refined by full matrix least squares in the anisotropic–isotropic (H atoms) approximation. The results of the refinement using 890 independent reflections with $I > 2\sigma(I)$ is $R_1 = 0·0536$, and for all 1426 measured reflections $wR_2 = 0·1446$ and $GOF = 0·979$. All calculations were performed with a PC/AT computer using the SHELX programs (version 3). The final atomic parameters for non-hydrogen atoms are listed in table 2; the values of important bond lengths and bond angles in the structure of MDCS are given in table 3.

Investigation of the phase transitions temperatures of MDCS was performed by the standard DSC method using a Perkin-Elmer DSC-7 calorimeter. The heating rate was 20° min^{-1}, with a temperature interval from −70 to +105°C.

4. Results and discussion

When analysing the conformational maps of the isolated molecules (figure 1), we assumed that if these maps for MDSO and MDCS were similar, the structural behaviour of these molecules would be nearly identical; on the other hand substantial differences in the conformational maps would be an indication of the different structural behaviour of MDSO and MDCS. Also, the investigation of the isolated molecules provides information about intramolecular hydrogen bond formation. We assume that if intramolecular H-bonds are present, formation of the liquid crystal phase will be less likely because of a decrease in rigidity of the H-bonded

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for MDCS.

Atom	*X*	*Y*	*Z*	*U*
Si(1)	1720(2)	5035(1)	5318(1)	23(1)
Si(2)	4880(3)	3569(1)	6677(1)	25(1)
O(1)	112(7)	3856(3)	5236(2)	32(1)
O(2)	6169(7)	3051(3)	5750(2)	28(1)
C(1)	3372(11)	4975(5)	6395(3)	25(1)
C(11)	−188(14)	6331(6)	5377(5)	37(1)
C(12)	2936(14)	2407(6)	7035(5)	41(2)
C(21)	3507(12)	5119(6)	4282(4)	37(2)
C(22)	6965(13)	3825(7)	7587(4)	41(2)

Table 3. Bond lengths (Å) and bond angles (°) for MDCS.

Bond length			
Si(1)–O(1)	1·649(5)	Si(2)–O(2)	1·660(4)
Si(1)–C(21)	1·849(6)	Si(2)–C(12)	1·830(7)
Si(1)–C(1)	1·853(5)	Si(2)–C(22)	1·840(7)
Si(1)–C(11)	1·860(7)	Si(2)–C(1)	1·875(7)

Bond angles			
O(1)–Si(1)–C(21)	108·6(3)	O(2)–Si(2)–C(12)	105·7(3)
O(1)–Si(1)–C(1)	110·0(2)	O(2)–Si(2)–C(22)	109·0(3)
C(21)–Si(1)–C(1)	112·6(3)	C(12)–Si(2)–C(22)	109·8(3)
O(1)–Si(1)–C(11)	106·6(3)	O(2)–Si(2)–C(1)	110·2(2)
C(21)–Si(1)–C(11)	110·5(4)	C(12)–Si(2)–C(1)	111·6(4)
C(1)–Si(1)–C(11)	108·4(3)	C(22)–Si(2)–C(1)	110·4(3)
Si(1)–C(1)–Si(2)	118·1(3)		

skeleton. This assumption can be partly confirmed by the structure of the *iso*-Pr substituted dihydroxydisiloxane, in which dimers are linked together by one H-bond only and the other three H-bonds are intradimeric bonds (scheme 2). The conformational maps shown in figure 1 indicate the similarity of the maximum and minimum $E(\omega_1;\omega_2)$ positions, i.e. that the most advantageous conformations of these molecules are identical. The difference between MDSO and MDCS is in their barriers of rotation about the X–Si(1, 2) bonds. The values of the transition barriers $E(\omega_1;\omega_2)\rightarrow E(\omega_3;\omega_2)$ (when $\omega_2=\text{const}$) for MDSO are significantly lower than those for MDCS:

Transition	E_{MDSO}/ kcal mol^{-1}	E_{MDCS}/ kcal mol^{-1}
$E(60;120)\rightarrow E(180;120)$	0·9	3·8
$E(60;180)\rightarrow E(180;180)$	0·6	2·2

This might be explained by the conformational flexibility of Si–O–Si fragments relative to Si–C–Si fragments, which was discussed elsewhere [15].

The global minima of the conformational energy corresponds to the torsion angles which are preferable for intramolecular H-bond formation. For the MDSO molecule the difference between the energies of global and local minima is *c*. 0·5 kcal mol^{-1}, and for the MDCS molecule is *c*. 0·5 kcal mol^{-1}. The correlation of these values is of the same order as the correlation of the barriers of conformational transitions between these minima, so the relative preference of intramolecular H-bond formation for both molecules is nearly the same. In contrast with the results of conformational calculations, X-ray data for the MDSO molecule does not show the formation of intramolecular hydrogen bonds. This result shows the domination of intramolecular interactions (including H-bond formation) for MDSO molecules. So we suppose a similar conformational behaviour holds for MDCS molecules.

Analysis and comparison of the MDSO and MDCS H-bonded associates also shows the similarity of the structural behaviour of these associates. The conformational energies of the *a* and *b* dimers are close to

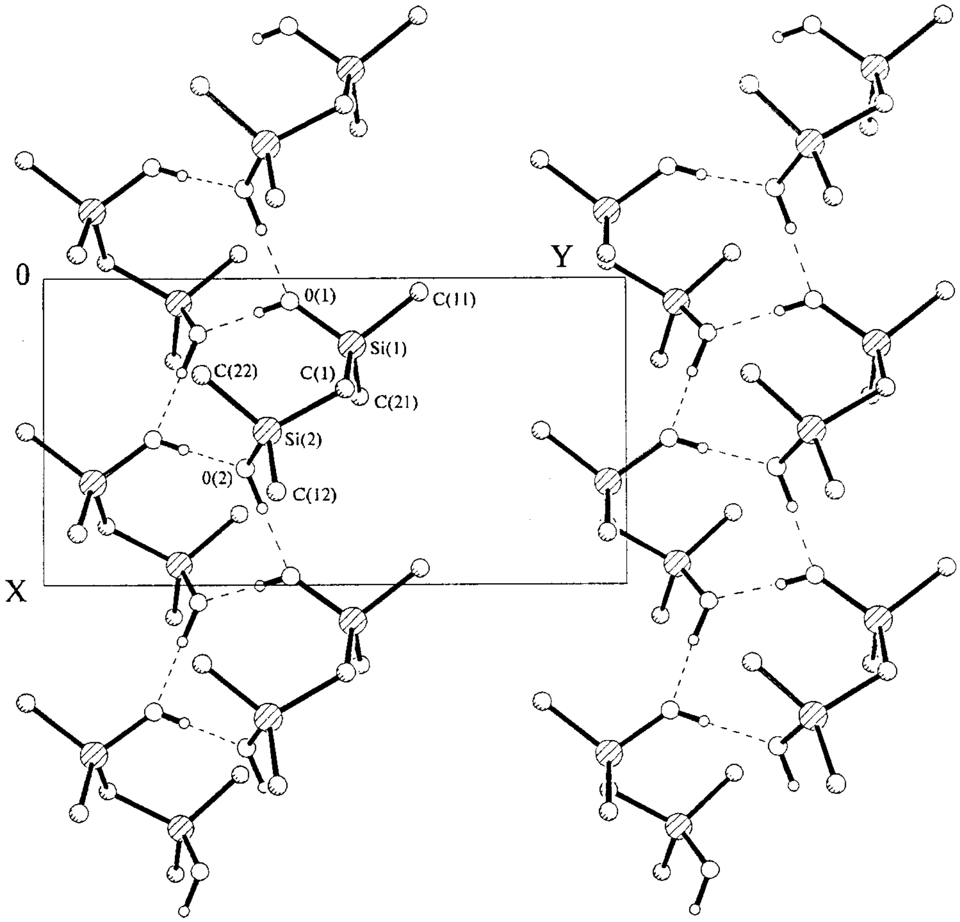


Figure 4. Packing diagrams for MDCS showing molecular chains (columns) along the X axis (projection on *ab* plane). Hydrogen bonds are shown by broken lines.

each other, and probably correspond to the local minima on the conformational potential energy surface. Without taking into account the influence of the crystal environment, further analysis of the dimers does not seem to be useful.

Hence the results of MM calculations of the isolated MDSO and MSCS molecules and of their bimolecular associates demonstrate a strong resemblance of conformational properties and structure formation; these results support our previous speculation [10] on the possibility of formation by these molecules of one-dimensional H-bonded associates of a ribbon type. Experimental investigation of the MDCS structure revealed that our speculation on supramolecular structural organization of this compound was reasonable.

According to the results of single crystal X-ray analysis, the crystal structure of MDCS consists of infinite molecular chains, directed along the X axis (figure 4). They are formed by O(1)–H(1)... O(2) (−0·5+x, 0·5−y, 1−z), and O(2)–H(2)... O(1) (1+x, y, z) H-bonds with the following geometrical parameters: O(1)–H(1) 0·79(2) Å, H(1)... O(2) 1·88(2) Å, O(1)... O(2) 2·668(6) Å, the bond angle at the H(1) atom is equal to 166(1)°; O(2)–H(2) 0·93(2) Å, H(2)... O(1) 1·71(2) Å, O(2)... O(1) 2·633(6) Å, the bond angle at the H(2) atom is equal to 165(1)°. A slight elongation of the Si(2)–O(2) bond (1·660(4) Å) in comparison with the Si(1)–O(1) bond (1·649(5) Å) may be caused by the difference in strength of the O(1)–H(1)... O(2) (−0·5+x, 0·5−y, 1−z) (2·668(6) Å) and the O(2)–H(2)... O(1) (1+x, y, z) (2·633(6) Å) H-bonds. The pattern of hydrogen bonding in the MDCS crystal is the same as in alkyl-substituted DSO. The value of the Si–C–Si bond angle in the MDCS molecule (118·1°) differs from values of the Si–O–Si bond angles for the Alk-DSO (Alk = Me, Et, Pr) (140–167°). It should be mentioned that for all Alk-substituted DSO, one can see a trend of the increase of the Si–O–Si bond angle on going from Me- to *iso*-Pr-substitution [2]. Differences in the above mentioned angles might be explained, in our opinion, by the conformational flexibility of the Si–O–Si fragments [15, 16] (see above). The values of the O–Si... Si–O pseudo-torsion angles for the Alk-DSO molecules are between 70° and 96° [2]; this value for MDCS is equal to 85·6°. H-bonded chains of MDCS molecules have a nearly cylindrical form with a flexible alkyl 'surface'. These cylindrical assemblies are packed in pseudo-hexagonal arrays (figures 5 and 6).

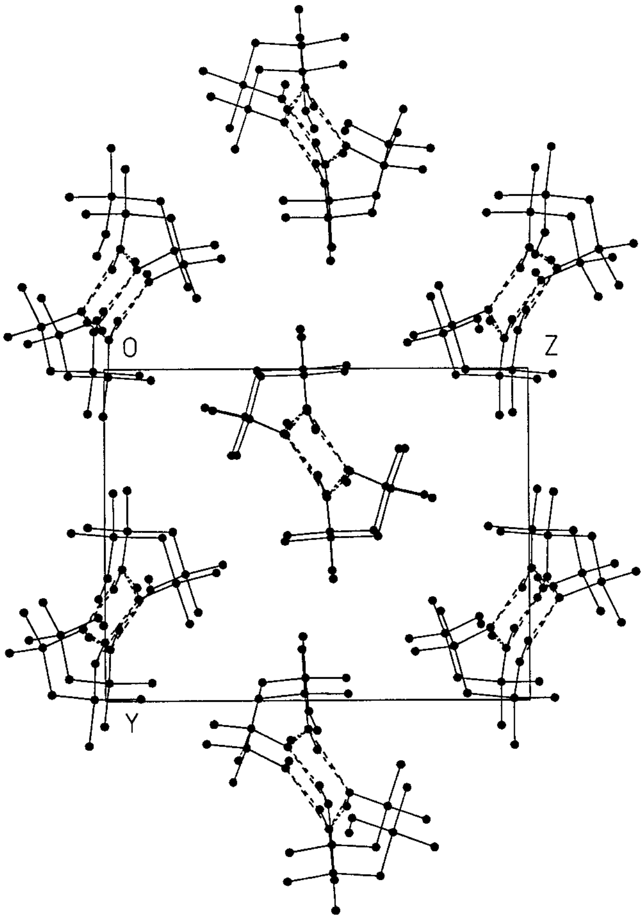


Figure 5. Pseudo-hexagonal packing of H-bonded chains of MDCS; projection on the *bc* plane.

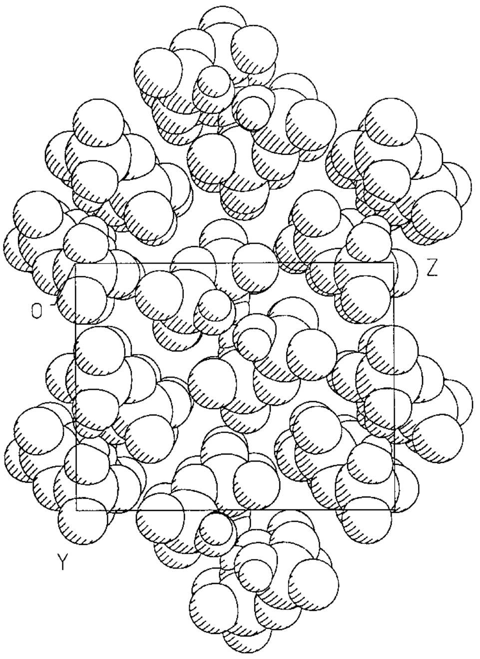


Figure 6. Pseudo-hexagonal packing of quasi-cylindrical molecular columns in the crystal structure of MDCS; projection on the *bc* plane.

It is important to mention that microscopic one-dimensional supramolecular associates are obviously reflected in the shape of MDCS crystals. As was mentioned above, MDCS crystals are thin needles elongated along the *a* axis, corresponding to the direction of the H-bonded associates.

Results of temperature-dependent x-ray measurements are shown in figure 7. Analysis of these data (curves *a*, *b*, and *c*) shows that MDCS possesses no polymorphic transitions. As the temperature increases from room to 70°C, no significant changes in the intensity and angular positions of reflections are observed. The only difference is related to a slight shift of the angular positions of the reflections, corresponding to thermal expansion. The beginning of the melting process is registered at 66°C (figure 7, curve *d*), and it lasts until near 83°C. Heating of the sample above the melting point of the crystallites results in the disappearance of all crystalline reflections and in the appearance of a quite different scattering pattern (figure 7, curve *e*). In the narrow temperature region ~83–85°C the pattern shows a weak but well-defined reflection at $2\Theta_m = 16{\cdot}28°$ ($d_m = 5{\cdot}4$ Å), with a

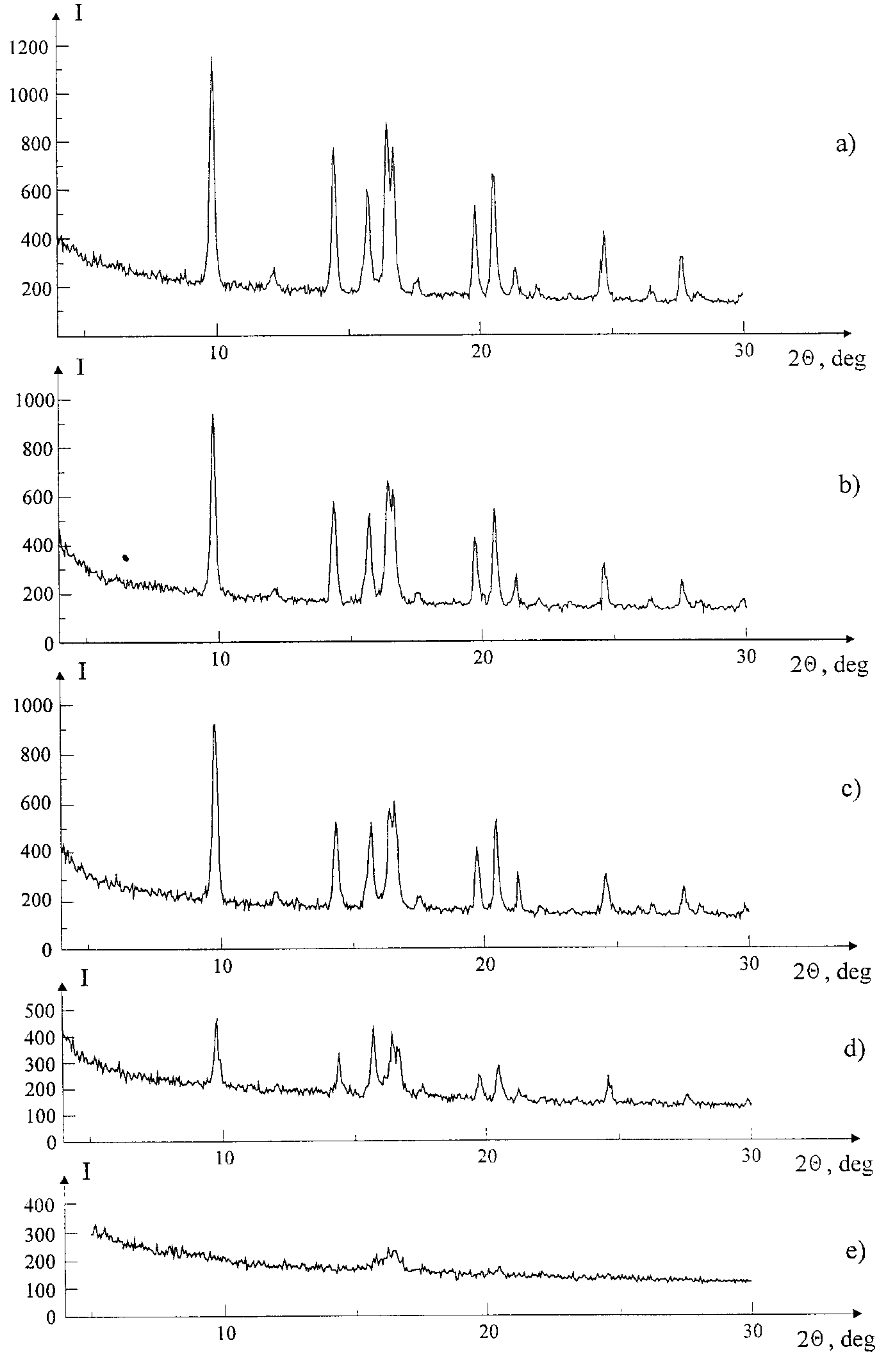


Figure 7. Diffraction scans of MDCS obtained at elevated temperatures: (*a*) 18°C; (*b*) 66°C; (*c*) 70°C; (*d*) 77°C; (*e*) 85°C.

half-width of $\sim\Delta_{1/2}=60'$. This evidence suggests the possibility of the existence of a mesophase above the melting temperature. The dimensions of the coherence regions are rather small (less than 150 Å). Hence, this ordered phase may be identified as a nematic or a nematic discotic (N_D) mesophase, but the exact type is uncertain. Investigations in the temperature region close to the melting point are restricted by sublimation of the sample. The existence of weakly pronounced order in the lateral direction can be proposed after comparison of the interplanar spacing d_m with the known dimensions of MDCS molecules and their possible hydrogen-bonded assemblies in the mesophase. This conclusion can be supported by the following: the mesophase diffraction maxima are located in the angular region $2\Theta_m$, which corresponds to the angular position of the most intensive Bragg reflection of the orthorhombic unit cell {0 2 1}. However, the other Bragg reflection of the orthorhombic unit cell, i.e. {1 1 0}, is located in the same regular region. So the exact nature of this mesophase is an open question.

On the DSC curves in the narrow temperature range above the melting point, a small endothermic transition was observed. This indicates mesophase formation above the melting point. Unfortunately the sublimation process complicated attempts at a more precise investigation.

5. Conclusion

According to our results, there are strong resemblances between the DSO and the DCS series in their molecular and supramolecular organization. It is very likely that the structures of the other alkyl-substituted DCS (for instance with Alk = Et, Pr, Bu) should be of the same type as the structure of MDCS, and using the analogy with DSO we can suppose that the region of the mesophase would be wider for these compounds and their experimental investigation would be easier.

The unusual system of H-bonds found in the MDCS and MDSO crystals suggests that the compounds which belong to both series might be useful for crystal engineering, for instance for one-dimensional parallel arrangements of guest molecules with special properties (for instance, nonlinear optical), which in the individual crystals have other relative orientations.

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