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Molecular Arrangements in Glycosphingolipids: The Crystal Structure of Glucosylphytosphingosine Hydrochloride

BY SIXTEN ABRAHAMSSON, BIRGITTA DAHLÉN AND IRMIN PASCHER

Department of Structural Chemistry, Faculty of Medicine, University of Göteborg, Fack, S-400 33 Göteborg 33, Sweden

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Glucosylphytosphingosine hydrochloride monohydrate ($C_{24}H_{50}ClNO_8.H_2O$), which represents a compound of the psychosine type, crystallizes in the space group $P2_12_12_1$ with $a = 11{\cdot}363\,(22)$, $b = 5{\cdot}262\,(17)$ and $c = 49{\cdot}71\,(17)$ Å. The molecules pack head-to-tail in pairs which are arranged in single layers. The hydrocarbon chains are tilted 42° to accommodate two chains per glucose residue and adopt the orthorhombic subcell packing $O\perp$. In adjacent layers the hydrocarbon chains show alternating tilt. The molecules are linked by a three-dimensional network of hydrogen bonds in which a water of crystallization plays an important role.

Introduction

Glycosphingolipids comprise a variety of important membrane lipids ranging from cerebrosides with a single carbohydrate residue to compounds with very complex carbohydrate patterns such as gangliosides and blood-group active oligoglycosylceramides (Wiegandt, 1971; Hakomori, 1973). These lipids are predominantly found in the plasma membranes and are considered to be cell-surface components involved in intercellular recognition and communication (Roth, 1973). A remarkable change in the glycosphingolipid pattern has been observed in transformed cells which is assumed to cause the aberrant surface function common to all tumour cells (Hakomori, 1973).

Cerebrosides represent the simplest structures among glycosphingolipids and a great number of species varying in carbohydrate, long-chain base and fatty acid composition exist in different organs of animals and plants (Karlsson, 1970; Karlsson, Samuelsson & Steen, 1973). The title compound belongs to a class of compounds known as psychosines, which constitute the carbohydrate–long-chain base structure of cerebrosides (Shapiro, 1969) and have been shown to be intermediates in the metabolism of these membrane lipids (Hammarström, 1972). Phytosphingosine-containing cerebrosides were originally found in wheat flour (Carter, Hendry, Nojima, Stanacev & Ohno, 1961) and leaves (Carter & Koob, 1969), and were thought to be specific for plants only (Carter & Hendrickson, 1963). Some ten years ago, however, these species were also detected in animal tissue (Karlsson, 1964) and have since been shown to be rather abundant in human (Karlsson & Mårtensson, 1968) and bovine kidney (Karlsson, Samuelsson & Steen, 1973) and in the digestive tract of different mammals (Breimer, Karlsson & Samuelsson, 1974; Okabe, Keenan & Schmidt, 1968). Phytosphingosine is found in cerebrosides in combination with both galactose or glucose, and normal or 2-hydroxy fatty acid. There is, however, a distinct preference for a combination with glucose and 2-hydroxy fatty acids in plants (Carter, Hendry, Nojima, Stanacev & Ohno, 1961), and also in animal tissue such as kidney (Karlsson, Samuelsson & Steen, 1973) and intestine (Breimer, Karlsson & Samuelsson, 1974), in which membranes are exposed to a pronounced physical stress. This tissue-specific distribution is therefore considered to be a reflexion of special physicochemical properties of phytosphingosine-containing glycosphingolipids which appear to arise from the increased content and the stereospecific orientation of hydroxyl groups (Smith, McKibbin, Karlsson, Pascher & Samuelsson, 1975). Because of the possibility that they may form lateral hydrogen bonds, these groups may contribute to an increase in stability and decrease in permeability of the membrane layers (Pascher, 1976).

The present paper describes the crystal structure analysis of glucosylphytosphingosine hydrochloride which was performed within the scope of an investigation on conformation, molecular arrangement, and hydrogen-bonding capability of sphingolipids and their molecular components (Abrahamsson, Pascher, Larsson & Karlsson, 1972; Pascher, 1976).

Experimental

Glucosylphytosphingosine [1-*O*-(β-D-glucopyranosyl)-D-*ribo*-3,4-dihydroxy-2-aminooctadecane] was synthesized from highly purified phytosphingosine from the yeast *Hansenula ciferrii* and α-acetobromoglucose according to the procedure described for galactosylphytosphingosine (Pascher, 1974).

The compound was converted into the hydrochloride by neutralization with hydrochloric acid, and crystallized from moist chloroform–methanol.

Crystal data

Molecular formula $C_{24}H_{50}ClNO_8.H_2O$, orthorhombic, $a = 11{\cdot}363\,(22)$, $b = 5{\cdot}262\,(17)$, $c = 49{\cdot}71\,(17)$ Å, $V = 2972$ Å^3. $M_r = 534{\cdot}13$, $Z = 4$, $D_c = 1{\cdot}19$, $D_m = 1{\cdot}19$ g cm^{-3}. Systematically absent reflexions: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. Space group $P2_12_12_1$. $\lambda = 1{\cdot}54051$ Å (Cu $K\alpha_1$ radiation), $\mu = 15{\cdot}14$ cm^{-1}.

A single crystal mounted with the b axis coinciding with the φ axis of the diffractometer was used for the data collection. Data were recorded on a Picker FACS1 automatic diffractometer with the Vanderbilt disc-oriented program system (Lenhert, 1975). Intensities up to $2\theta = 120°$ were measured with graphite-monochromated Cu $K\alpha$ radiation. The reflexions were scanned (θ–2θ) in 10 steps of 4 s with a step size of 0·2°. Stationary background counts (10 s) were taken on both sides of the peaks. 2650 reflexions were recorded. The Lorentz–polarization factor was applied but no corrections were made for absorption or extinction. Scattering factors for C, O, N and Cl atoms were those in *International Tables for X-ray Crystallography* (1962), and for H those of Stewart, Davidson & Simpson (1965) were used. The scattering curve for Cl was corrected for anomalous dispersion (Cromer & Liberman, 1970).

The calculations were performed on a Datasaab D21-PDP15 dual computer with programs developed at this laboratory, and later on a System DEC 10 with *MULTAN* (Germain, Main & Woolfson, 1971) and the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The programs have been modified for DEC10 by Dr Steve Ernst at the University of Pittsburgh and at this department by Dr Robert Pearson.

Structure determination and refinement

The structure was determined by direct methods with *MULTAN*. 182 reflexions with $|E| > 1{\cdot}3$ were used. The alternative with the highest figure of merit revealed the positions of the Cl atom and most atoms in the glucose ring.

The phases from these atoms were used in an electron density calculation which revealed all the other non-hydrogen atoms. The Fourier map also contained a large peak suggesting the presence of a water molecule, which was also compatible with the measured density.

The structure was refined by full-matrix least-squares methods. At first, reflexions with intensities $>2\sigma$ were used. For low intensities $|F_c|$ was systematically lower than $|F_o|$ which indicated that a higher cut-off value should be used. Measurements at systematically absent reflexions indicated 4σ as a suitable limit. This led to only 522 observed reflexions. Though rather large differences in the vibrational behaviour of the atoms were expected, isotropic temperature factors were used because of the relatively small number of reflexions. For the Cl atom, however, anisotropic temperature factors were applied. The structure refined to $R = 0{\cdot}099$.* All shift/error values were then less than

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32356 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates and isotropic temperature factors with standard deviations for the non-hydrogen atoms*

The chlorine atom is given anisotropic temperature factors in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

	$x(\times 10^3)$	$y(\times 10^3)$	$z(\times 10^4)$	$B(\times 10)$
Cl(1)	291 (1)	944 (3)	329 (3)	†
C(1)	621 (3)	355 (7)	763 (7)	16 (9)
C(2)	497 (3)	399 (9)	646 (8)	35 (10)
C(3)	428 (3)	562 (8)	853 (7)	19 (9)
C(4)	394 (3)	428 (9)	1112 (6)	12 (9)
C(5)	315 (3)	586 (8)	1287 (8)	31 (10)
C(6)	263 (3)	442 (9)	1530 (7)	36 (10)
C(7)	152 (3)	565 (8)	1640 (7)	21 (9)
C(8)	96 (3)	432 (9)	1875 (7)	34 (10)
C(9)	−13 (4)	561 (9)	1969 (8)	47 (11)
C(10)	−69 (4)	449 (10)	2230 (9)	57 (13)
C(11)	−184 (3)	547 (9)	2310 (8)	38 (10)
C(12)	−241 (4)	412 (10)	2558 (8)	46 (12)
C(13)	−356 (4)	551 (10)	2628 (9)	51 (12)
C(14)	−402 (3)	432 (9)	2885 (9)	52 (13)
C(15)	−518 (3)	535 (8)	2976 (8)	40 (11)
C(16)	−571 (4)	431 (11)	3245 (10)	74 (15)
C(17)	−679 (5)	553 (13)	3309 (13)	123 (23)
C(18)	−736 (5)	379 (12)	3537 (11)	98 (19)
O(1)	700 (2)	268 (7)	557 (5)	43 (7)
O(2)	488 (2)	809 (6)	910 (5)	29 (6)
O(3)	349 (2)	199 (6)	1036 (5)	2 (17)
N(1)	519 (2)	565 (7)	410 (6)	35 (18)
C(1′)	768 (3)	77 (9)	616 (7)	26 (10)
C(2′)	823 (2)	−46 (8)	360 (7)	13 (8)
C(3′)	919 (2)	−236 (7)	420 (6)	13 (7)
C(4′)	1018 (4)	−125 (9)	615 (8)	42 (12)
C(5′)	947 (3)	−12 (9)	853 (8)	28 (9)
C(6′)	1023 (3)	135 (8)	1053 (7)	32 (10)
O(2′)	722 (2)	−152 (6)	222 (5)	37 (7)
O(3′)	975 (2)	−297 (6)	170 (5)	28 (7)
O(4′)	1096 (2)	−282 (7)	685 (5)	53 (9)
O(5′)	864 (2)	178 (6)	778 (5)	34 (17)
O(6′)	1118 (2)	263 (6)	934 (5)	44 (8)
O(4)	90 (2)	284 (6)	35 (4)	21 (6)

† $U_{11} = 0{\cdot}031\,(5)$, $U_{22} = 0{\cdot}088\,(12)$, $U_{33} = 0{\cdot}082\,(9)$, $U_{12} = 0{\cdot}003\,(9)$, $U_{13} = -0{\cdot}016\,(7)$, $U_{23} = 0{\cdot}001\,(10)$.

0·01. The weighting scheme used during the last cycles of refinement was $w = 1/\{1 + [(|F_o| - 20)/50]^2\}$. All H atoms attached to C atoms were included at their calculated positions 1·09 Å from the parent C atoms. Attempts to locate the hydroxyl H atoms from difference Fourier maps were unsuccessful.

Description of the structure

The positional parameters are given in Tables 1 and 2. The atom numbering and the interatomic distances and angles are shown in Figs. 1 and 2. The mean C–C bond distance in the phytosphingosine chain is 1·52 (4) Å and the mean C–C–C angle in the chain is 113 (4)°, in good agreement with values previously found in long hydrocarbon chain compounds (Dahlén & Pascher, 1972).

The molecular packing is illustrated in Fig. 3 and the molecular conformation by a stereoscopic pair in Fig. 4. The molecules are arranged 'head-to-tail' in pairs to allow a packing of two hydrocarbon chains per glucose residue. This gives rise to fairly extended regions of van der Waals interaction between the chains of these 'head-to-tail' pairs of molecules. The relative translation of adjacent pairs in the carbon-chain direction is, however, such that only short parts of their chains are in contact laterally. In each pair the methyl end group C(18) is in contact with the glucose ring [C(5′) 3·91 Å] and the rather deformed polar end of the phyto-

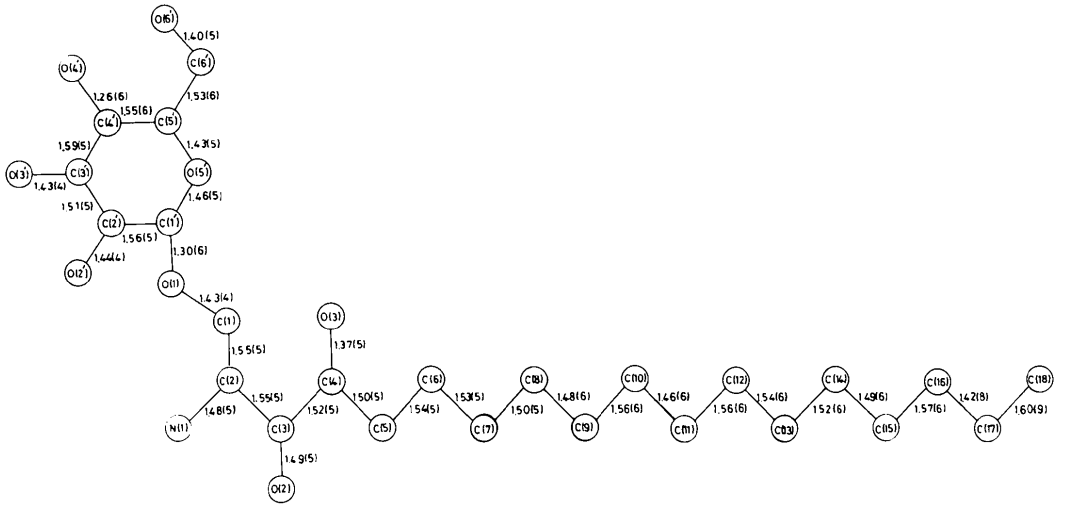

Fig. 1. Bond distances (Å) in glucosylphytosphingosine.

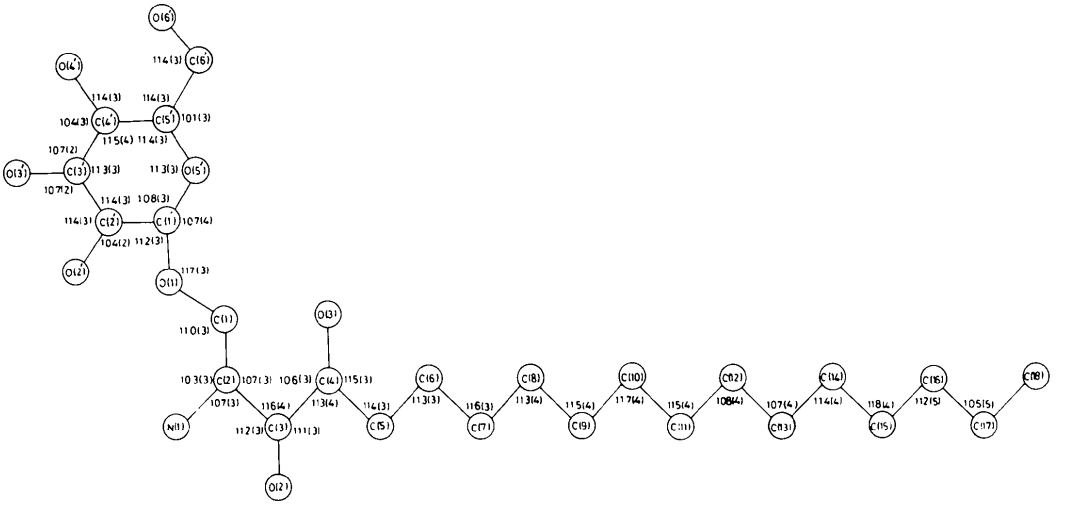

Fig. 2. Bond angles (°) in glucosylphytosphingosine.

Table 2. *Fractional atomic coordinates and isotropic temperature factors for the hydrogen atoms*

	x ($\times 10^3$)	y ($\times 10^3$)	z ($\times 10^4$)	B
H(11)	657	564	799	1·6
H(12)	625	260	939	1·6
H(21)	459	205	613	3·5
H(31)	356	636	727	1·9
H(41)	471	418	1234	1·2
H(51)	230	635	1178	3·1
H(52)	351	756	1366	3·1
H(61)	247	239	1480	3·6
H(62)	337	431	1691	3·6
H(71)	186	759	1708	2·1
H(72)	99	592	1469	2·1
H(81)	76	245	1783	3·4
H(82)	164	412	2022	3·4
H(91)	13	753	2022	4·7
H(92)	−76	556	1813	4·7
H(101)	−74	229	2183	5·7
H(102)	−2	457	2390	5·7
H(111)	−170	740	2342	3·8
H(112)	−242	510	2137	3·8
H(121)	−250	216	2524	4·6
H(122)	−177	444	2729	4·6
H(131)	−345	743	2653	5·1
H(132)	−419	501	2469	5·1
H(141)	−412	222	2860	5·2
H(142)	−334	457	3044	5·2
H(151)	−500	745	3011	4·0
H(152)	−578	521	2811	4·0
H(161)	−583	228	3195	7·4
H(162)	−510	459	3394	7·4
H(171)	−663	709	3395	12·3
H(172)	−737	517	3153	12·3
H(181)	−687	383	3724	9·8
H(182)	−761	191	3483	9·8
H(183)	−823	487	3584	9·8
H(17)	580	470	269	3·5
H(18)	554	741	474	3·5
H(19)	434	590	305	3·5
H(1′)	711	−26	752	2·6
H(2′)	858	83	230	1·3
H(3′)	868	−408	488	1·3
H(4′)	1075	−17	509	4·2
H(5′)	906	−181	912	2·8
H(61′)	977	235	1194	3·2
H(62′)	1075	−27	1179	3·2

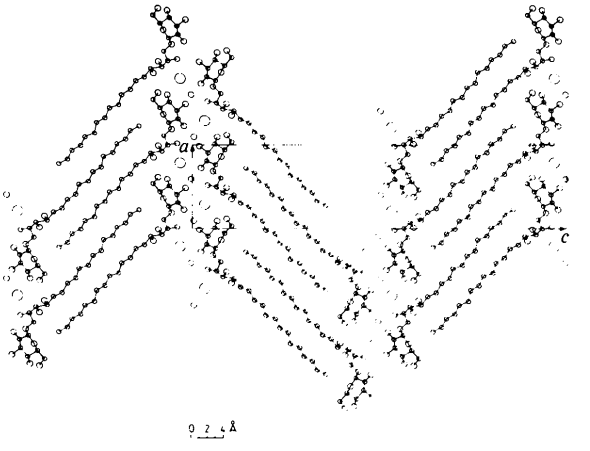

Fig. 3. Molecular packing of glucosylphytosphingosine hydrochloride as seen along **b**.

sphingosine chain of the other molecule. Furthermore, O(6′) of the glucose ring is in contact with C(5) (3·31 Å) of the chain of the molecule in an adjacent pair.

Despite this, the hydrocarbon chain is planar from C(5) to C(18) within 0·1 Å. A zigzag conformation continues further through the atoms C(4), C(3), C(2) and N(1) which lie in a plane within 0·01 Å. However, the orientation of this plane deviates from the main-chain plane by 29°.

Thus the N atom rather than C(1) lies in the direction of the phytosphingosine chain. This conformation is also found in sphingosine hydrochloride (Nilsson & Pascher, 1977). The angle of tilt of the chain axes to the end-group planes is 73° in sphingosine hydrochloride, whereas the bulky sugar residue in the present compound requires the larger tilt of 42°. In the corresponding psychosine species containing galactosylsphingosine, which also crystallizes in space group $P2_12_12_1$ with $a = 9{\cdot}91$, $b = 10{\cdot}01$ and $c = 69{\cdot}8$ Å, the tilt of the chains has been estimated to be about 62° (Abrahamsson, Pascher, Larsson & Karlsson, 1972).

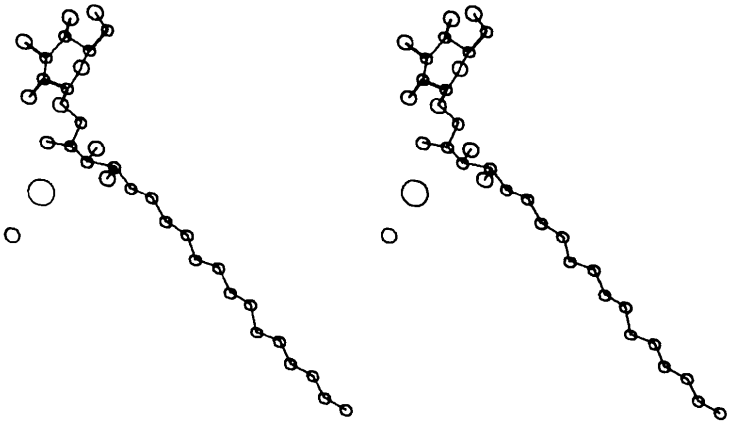

Fig. 4. Stereoscopic drawing of glucosylphytosphingosine hydrochloride.

The lateral packing in the regular part of the hydrocarbon matrix can be described by the common orthorhombic subcell $O\perp$ with dimensions $a_s = 5{\cdot}26$, $b_s = 7{\cdot}54$ and $c_s = 2{\cdot}53$ Å. The cross-section area per chain is 19·8 Å^2, which is large but not unexpected in a structure with the chain packing affected by large polar groups. A still higher value (20·9 Å^2) is found in the structure of sodium dodecylsulphate (Sundell, 1977).

The torsion angles between the substituents in the polar part of the phytosphingosine chain are found in Fig. 5. The conformation about the C(2)–C(3) and C(3)–C(4) bonds is identical with that in *N*-tetracosanoylphytosphingosine (Dahlén & Pascher, 1972) with a synclinal (−52°) and antiplanar conformation (−176°) between N(1) and O(2) and O(2) and O(3) respectively. The synclinal orientation of N(1) to O(2) about the C(2)–C(3) bond is also found in sphingosine hydrochloride. About the C(1)–C(2) bond O(1) and N(1) adopt a torsion angle of −52° in the psychosine and −53° in the sphingosine, whereas the corresponding value in the ceramide is 154°.

The β-D-glucose part of the molecule shows the normal chair conformation (Ferrier, 1963). Torsion angles illustrating the linkage between the phytosphingosine and the glucose, and the orientation of the primary hydroxyl oxygen at C(6′) are given in Fig. 6.

The environment of the chloride ion and the hydrogen-bond system are shown in Fig. 7. The chloride ion is roughly octahedrally surrounded by close neighbours. Four O atoms and a N atom lie at distances between 3·07 and 3·34 Å, whereas the sixth corner is occupied by C(3) at 3·64 Å.

The hydrogen-bonding system links the molecules effectively together in a three-dimensional network. The water molecule [O(4)] plays an important role being involved in four hydrogen bonds. The O atoms of the glucose take part in hydrogen bonds both to oxygens in sugar rings and in phytosphingosine of translated molecules and to the chloride ion. The glycosidic O(1) is in intramolecular close contact with the ammonium N. Of the hydroxyl groups in the phytosphingosine part, O(2) binds to O(3) of a **b** translated molecule whereas O(3) is hydrogen-bonded to O(6′) in an **a** translated molecule.

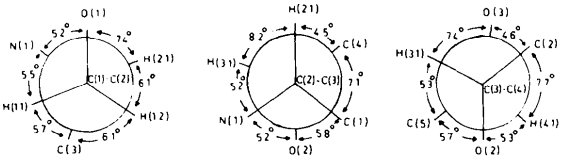

Fig. 5. Torsion angles (°) in the polar part of the phytosphingosine residue.

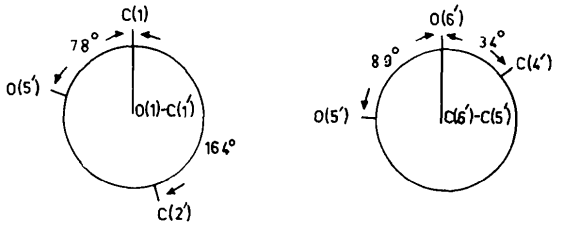

Fig. 6. Torsion angles (°) illustrating the glycosidic linkage and the orientation of the primary alcohol oxygen.

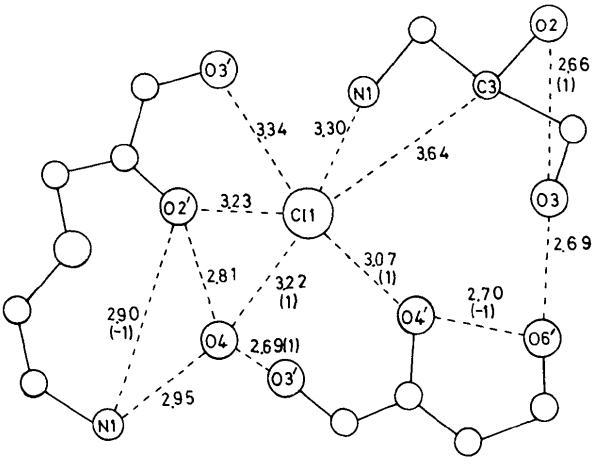

Fig. 7. Schematic illustration of the environment of the Cl atom.

In spite of the varying local environments in crystals of the different sphingosine compounds so far studied, the polar groups [N, O(2), O(3)] show identical conformations. This indicates the predominance of intramolecular forces as conformation-determining factors and allows general conclusions to be drawn on the preferred conformation of sphingolipids. A more detailed discussion and review of sphingolipid components studied within this project is given by Pascher (1976).

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The Crystal Structures of 1,3,5-Trimethylbenzenetricarbonylmolybdenum and Hexamethylbenzenetricarbonylmolybdenum

BY D. E. KOSHLAND, S. E. MYERS AND J. P. CHESICK*

Department of Chemistry, Haverford College, Haverford, Pennsylvania 19041, *USA*

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The crystal and molecular structures of 1,3,5-trimethylbenzenetricarbonylmolybdenum, $C_{12}H_{12}O_3Mo$ (TMB), and hexamethylbenzenetricarbonylmolybdenum, $C_{15}H_{18}O_3Mo$ (HMB), have been determined from diffractometer data. For both compounds the unit cell is monoclinic, space group $P2_1/c$, with $Z = 4$. For TMB, $a = 8{\cdot}8602\,(6)$, $b = 17{\cdot}090\,(4)$, $c = 9{\cdot}0368\,(7)$ Å, $\beta = 118{\cdot}788\,(5)°$, $R = 0{\cdot}037$ for 1789 observed reflections. For HMB, $a = 8{\cdot}9578\,(6)$, $b = 13{\cdot}688\,(10)$, $c = 14{\cdot}049\,(10)$ Å, $\beta = 121{\cdot}529\,(5)°$, $R = 0{\cdot}041$ for 2186 observed reflections. The molecules have close to C_{3v} symmetry, with methyl carbons displaced out of the benzene ring plane away from the $Mo(CO)_3$ group by 0·035 (5) (TMB) and 0·060 (8) Å (HMB). For TMB the carbonyl groups are eclipsed with respect to the benzene methyl C atoms. For HMB the carbonyl groups are staggered with respect to the benzene ring atoms, and the ring symmetry is reduced to C_{3v} with average short and long C–C bonds in the ring of 1·405 (5) and 1·441 (9) Å. Mo–C(aromatic) average distances are 2·372 (5) (TMB) and 2·392 (5) Å (HMB).

Introduction

Olefin complexes of Cr, Mo and W have been the subject of numerous structural reports, as reviewed, for example, by Quinn & Tsai (1969). Although many structures have been reported for π-cyclopentadienyl and π-cycloheptatrienyl complexes of Mo, structure determinations of π complexes of benzene or benzene derivatives with Mo have been scarce to nonexistent. Distortion of arene geometry by π complexation has also been a structural question. A variety of efforts to decide this issue for dibenzenechromium have been reviewed by Bailey & Dahl (1965*a*) in the context of their study of hexamethylbenzenetricarbonylchromium. This work of Bailey & Dahl showed some indication of displacements of the methyl C atoms away from the Cr atom. However, their values for the ring C–C bond lengths showed appreciable scatter (a sample standard deviation from the mean of 0·036 Å) and were therefore not sufficiently precise to show regular ring distortions of 0·05 Å or less. Bailey & Dahl (1965*b*) also reported a study of benzenetricarbonylchromium in which the averages of the three 'long' and three 'short' bonds in the ring were identical to within the least-squares e.s.d. of 0·01 Å for each bond. The recent careful low-temperature studies by X-ray and neutron diffraction of $(C_6H_6)Cr(CO)_3$ by Rees & Coppens (1973) definitely showed reduction of the benzene ring symmetry to C_{3v}, with a 0·02 Å alternation in bond lengths and the H atoms displaced 0·03 Å from the plane of the ring *towards* the Cr atom.

* To whom correspondence should be addressed.