Molecular Mechanics Calculations for Ethers. The Conformations of Some Crown Ethers and the Structure of the Complex of 18-Crown-6 with Benzylammonium Thiocyanate

By **Moira J. Bovill, Derek J. Chadwick,** and **Ian O. Sutherland,*** Department of Organic Chemistry, The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX
(in part) **David Watkin,** Chemical Crystallography Laboratory, Parks Road, Oxford OX1 3PD

The White–Bovill alkane–alkene force field (WBFF) has been slightly modified and extended for the calculation of geometrical and thermodynamic properties of saturated compounds containing the isolated ether or the 1,4-dioxa grouping. The new force field reproduces the heats of formation of 14 ethers with a mean deviation of 0.86 kcal mol^{-1} between observed and calculated enthalpies. Bond lengths, bond angles, and torsion angles are satisfactorily reproduced with mean deviations of 0.010 Å, 1.0°, and 4.3° respectively over a set of 103 observations. The force field has been used to investigate the detailed relationship between the strain energies and the corresponding equilibrium geometries of various conformations of 9-crown-3, 12-crown-4, and 18-crown-6. The determination of the structure of the complex of 18-crown-6 with benzylammonium thiocyanate, by *X*-ray crystallography, is described and molecular mechanics calculations are used to comment upon the conformations adopted by 18-crown-6 in a range of complexes.

THE molecular mechanics (MM) method is now being used to an ever increasing extent by chemists to calculate geometric, spectroscopic, and thermodynamic properties of organic molecules.[1-5] The method is, however, somewhat limited because reliable calculations can only be performed on compounds for which carefully parameterised force fields already exist, for example alkanes,[3,6,7] alkenes,[7,8] some aromatic compounds,[9] and aldehydes and ketones.[10] In addition, attempts have been made to tackle the rather more difficult problems posed by conjugated systems [11] and force fields exist for halides [12] and alcohols and ethers [13] which require modification in the light of recent developments.[6b]

Our investigation [14] of the chemistry of complexes formed by crown ethers and analogous macrocyclic compounds has generally been based upon conformational information derived from studies of molecular models or from crystal structure data. If the MM method is to be used as a basis for these studies it is clearly necessary that existing force fields must be considerably developed, particularly with respect to the inclusion of ether and amino groups in the parameterisation. This paper reports the development of a new force field for the calculation of geometric and thermodynamic properties of saturated compounds containing an isolated ether group. It has also been used for the 1,4-dioxa grouping, characteristic of crown ethers.

The Force Field.—The White–Bovill force field (WBFF) [7] for alkanes and non-conjugated alkenes is one of the most reliable of its type and it reproduces enthalpies and geometries with an accuracy comparable with that of experimental methods. Thus the mean deviation between calculated and observed heats of formation and hydrogenation over 60 diverse alkanes and alkenes is 0.55 kcal mol^{-1} and the mean deviations for bond lengths, bond angles, and torsion angles are 0.009 Å, 0.6°, and 0.9°, respectively, over a set of 93 observations.

A re-investigation of WBFF has, however, revealed a defect in that the ring inversion barrier in cyclohexane was calculated to be too low by 2.8 kcal mol^{-1}. This has now been remedied by increase in the heights of the torsional barriers about H–C(sp^3)–C(sp^3)–H and H–C(sp^3)–C(sp^3)–C(sp^3) from 0.110 0 to 0.165 8 kcal mol^{-1} and about C(sp^3)–C(sp^3)–C(sp^3)–C(sp^3) from 0.062 9 to 0.165 8 kcal mol^{-1}. This new version of the WBFF will be referred to as WBFF2 (see Table 1) and will be used in all future extensions of the force field. WBFF2 predicts geometric properties as reliably as the former version of the force field but the thermodynamic properties are predicted slightly less accurately than previously. Thus the mean deviation between the calculated and observed heats of formation and hydrogenation is now 0.66 kcal mol^{-1} over 60 compounds. A list of results from MM calculations using WBFF2 is available on request. We note the value of inversion barriers for six-membered rings [15] as a guide to the correct assessment of the magnitudes of torsional barriers about single bonds in the ring: this method has also proved useful for the estimation of parameters for torsional barriers in the ether force field described below. Details of the transition states for ring inversion are given in Table 7.

The alkane–alkene WBFF2 (Table 1) was used without alteration for the development of a force field to allow MM calculations for the prediction of geometries and enthalpies of saturated compounds containing one or more ether groups.† The description of the electron density around an oxygen atom in MM calculations has given rise to much discussion. For example, the electron density about the oxygen atom may be considered to be spherical and centred on the nucleus [16] or the lone pairs of electrons may be treated explicitly.[13,17] The general philosophy of MM calculations is to adopt the simplest

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† The 1,3-dioxa grouping requires a further extension of the force field developed in this paper (*cf.* ref. 13), it should not therefore be used for compounds containing this group. Furthermore, since none of the reference compounds contain oxygen atoms with a high degree of steric crowding there is a need for an investigation of the conformations of compounds in which such interactions are unavoidable.

TABLE 1

Force field parameters for alkane–alkene force field WBFF2

Atom key: 1 = H, 2 = C(sp^2), 3 = C(sp^3). Force constants are in kcal mol^{-1} Å^{-2} or in kcal mol^{-1} deg^{-2}; energies are in kcal mol^{-1}

Bond stretching

Type 1	Type 2	$1/2k_l$	l_0
1	2	346.0	1.089
1	3	331.2	1.100
2	2	670.0	1.335
2	3	319.5	1.501
3	3	316.8	1.520

van der Waals

Type 1	Type 2	r_1*	r_2*	ε
1	1	3.10	0.0	0.0160
1	2	3.53	0.0	0.0330
1	3	3.35	0.0	0.0299
2	2	4.00	0.0	0.0760
2	3	3.60	0.0	0.0800
3	3	3.85	0.0	0.1200

Angle bending

Type 1	Type 2	Type 3	$1/2k_\theta$	k^1_θ	θ^1_o*	θ^2_o	θ^3_o	θ^4_o
1	2	1	0.0055	0.0096	118.6			
1	2	2	0.0060	0.0	121.7	120.4		
1	2	3	0.0060	0.0		117.5		
2	2	3	0.0120	0.0096		122.3	121.0	
3	2	3	0.0233	0.0096			116.4	
1	3	1	0.0072	0.0096	108.2	109.1		
1	3	2	0.0088	0.0096	110.5	110.0	110.2	
1	3	3	0.0088	0.0096	109.0	109.2	109.2	
2	3	2	0.0090	0.0096		111.0	110.1	109.5
2	3	3	0.0090	0.0096		110.4	110.1	109.5
3	3	3	0.0120	0.0096		110.4	110.1	109.5

Torsion

Type 1	Type 2	Type 3	Type 4	$1/2k_\omega$	s	n
1	2	2	1	6.2500	−1.0	2.0
1	2	2	3	6.2500	−1.0	2.0
3	2	2	3	6.2500	−1.0	2.0
1	2	3	1	0.1367	1.0	3.0
1	2	3	2	0.1367	1.0	3.0
1	2	3	3	0.1367	1.0	3.0
2	2	3	1	0.0629	−1.0	3.0
2	2	3	2	0.0629	−1.0	3.0
2	2	3	3	0.0629	−1.0	3.0
3	2	3	1	0.0629	1.0	3.0
3	2	3	2	0.0629	1.0	3.0
3	2	3	3	0.0629	1.0	3.0
1	3	3	1	0.1658	1.0	3.0
1	3	3	2	0.1100	1.0	3.0
1	3	3	3	0.1658	1.0	3.0
2	3	3	2	0.0200	1.0	3.0
2	3	3	3	0.0629	1.0	3.0
3	3	3	3	0.1658	1.0	3.0

Out-of-plane bending

Type 1	Type 2	Type 3	Type 4	$1/2k_\chi$
3	2	2	1	0.0020
3	2	2	3	0.0020

Group enthalpy increments (kcal mol^{-1})

Group	Increment	E.s.d.
=CH$_2$	6.33	0.21
=CH	8.55	0.08
=C	9.94	0.36
−CH$_3$	−10.31	0.11
−CH$_2$	−5.51	0.05
−CH	−2.29	0.08
−C	−0.88	0.25

* Superscript indicates the degree of substitution at the central atom.

model, with the minimum number of necessary adjustable parameters, consistent with the available experimental data. We therefore treated the oxygen atom as spherical at the outset of our parameterisation with the proviso that an explicit treatment of lone pairs of electrons could be introduced at a later stage, if required. In the event the spherical atom model reliably reproduced the experimental data considered in this paper; this does not, however, preclude the introduction of lone pair electrons for situations other than those considered here.†

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† The 1,3-dioxa grouping requires a further extension of the force field developed in this paper (*cf.* ref. 13), it should not therefore be used for compounds containing this group. Furthermore, since none of the reference compounds contain oxygen atoms with a high degree of steric crowding there is a need for an investigation of the conformations of compounds in which such interactions are unavoidable.

For molecules that contain two or more heteroatoms, it is necessary to consider the electrostatic interactions which occur between them, in addition to the normal non-bonded interactions described by the usual non-bonded interatomic potential functions. The electrostatic interactions may conveniently be included by treatment of each heteroatom as an electric monopole having a partial charge e; the directly adjacent carbon atoms must then carry charges that sum to equal that on the heteroatom so that a neutral molecule is produced. The molecular potential energy due to the resulting coulombic interactions, E_Q, may then be calculated from relationship (1)[19] where e_i and e_j are

$$E_Q = 332.17(\sum_{ij} e_i e_j / r_{ij} \cdot D)\ \text{kcal mol}^{-1} \qquad (1)$$

the partial charges on atoms i and j, derivable from molecular orbital calculations, D is the dielectric constant[*] and r_{ij} is the interatomic distance between atoms i and j in Å.

TABLE 2

Additional parameters required for ether force field

Atom key: 1 = H, 3 = C(sp^3), 5 = —O—. Force constants are in kcal mol^{-1} Å^{-2} or in kcal mol^{-1} deg^{-2}; energies are in kcal mol^{-1}

Bond stretching

Type 1	Type 2	$1/2k_1$	I_0
3	5	400.0	1.412

van der Waals

Type 1	Type 2	r_1 *	r_2 *	ε
3	5	3.50	0.0	0.2000
5	5	3.40	0.0	0.0800
1	5	3.15	0.0	0.0110

Angle bending

Type 1	Type 2	Type 3	$1/2k_\theta$	k_θ^1	θ^1_0 *	θ^2_0	θ^3_0	θ^4_0
1	3	5	0.0088	0.0096	109.0	109.2	109.2	
3	3	5	0.0118	0.0096		109.0	109.0	109.0
3	5	3	0.0160	0.0096		109.5		

Torsion

Type 1	Type 2	Type 3	Type 4	$1/2k_\omega$	s	n
5	3	3	5	0.4000	1.0	3.0
3	5	3	1	0.4000	1.0	3.0
1	3	3	5	0.1950	1.0	3.0
3	3	3	5	0.0629	1.0	3.0
3	5	3	3	0.2000	1.0	3.0

Charges (in units of e, the electronic charge)

—O— (ether)	−0.300e
—C—	+0.150e

* Superscript indicates the degree of substitution at the central atom.

The analytical forms of potential functions used to describe bond length deformation, bond angle bending, bond torsion, and non-bonded interactions in the new ether force field were identical to those used in the development of WBFF.[7] The optimum values for the force constants and reference geometries for the 2-, 3-, and 4-atom interactions of the oxygen atom with the carbon, hydrogen, and other oxygen atoms were obtained by a trial and error process of parameterisation;[7] the resulting values are given in Table 2.

Values for the non-bonded atomic radii and ε for the O · · · O interactions were particularly difficult to determine owing to the paucity of relevant experimental data. Initially, the oxygen atom was treated as being small in size and relatively hard and accordingly the sum of the van der Waals radii was taken as 2.80 Å and ε as 0.385 0. However, because this model did not seem physically reasonable, the sum of the van der Waals radii was increased to 3.40 Å and ε was decreased to 0 080 0. Surprisingly, this change had little effect on the reliability of the calculations; the only marked difference being that the first version of the ether force field, utilising a small and hard O · · · O non-bonded interaction, predicted that the *trans,trans,trans*-isomer and the *trans,gauche,trans*-isomer of 1,2-dimethoxyethane are isoenergetic whereas the final version of the force field indicates that the *trans-trans-trans*-isomer is more stable by 0.44 kcal mol^{-1}. Electron diffraction experiments[20] imply that the equilibrium mixture of conformations of 1,2-dimethoxyethane is composed mainly of the *trans,trans,trans*-, *trans,gauche,trans*-, and *trans,gauche,gauche*-conformers, in accord with predictions from both versions of the ether force field (Table 5).

Tables 3—5 list the comparisons between observed and calculated structural parameters, heats of formation, and conformational energies respectively, for saturated ethers. Values for the oxygen group enthalpy increments, which are utilised, in conjunction with the alkane–alkene group enthalpy increments,[7] to calculate the heat of formation ΔH_f^0 (gas; 25 °C) of a particular ether, are

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[*] The assessment of an interatomic dielectric constant is not straightforward; we have used the value 5 by analogy with previous work[18] and on the basis of ΔH_f^0 of 1,4-dioxan; in any case the value chosen is not critical since electrostatic interactions represent a relatively small part of the interatomic non-bonded interactions.

derived by a linear least-squares method and are reported in Table 6. Five increments were evaluated since the –O–(CH_2) increment in oxetan was treated separately from the –O–(CH_2) increment in the other compounds on account of the excessive steric energy in the former. The energy minimisation algorithms and general procedure were the same as those used in the development [7] of the WBFF.

RESULTS AND DISCUSSION

The amount of experimental data in the chemical literature which are of potential use in force field development is more scarce for ethers than for alkanes and alkenes. Nevertheless it is believed that the new ether force field, summarised in Tables 1 and 2, is sufficiently well defined for confidence to be placed in its predictions, although to a lesser extent than in the case of the alkane–alkene WBFF.[7] There is, however, an adequate body of information on which the C–O bond length, and the C–O–C and the O–C–C bond angles, may be based. The force field predicts accurately (Table 5) the ring inversion barrier in 1,4-dioxan and in tetrahydropyran, the torsional barrier in dimethyl ether, the conformational energies for diethyl ether and methoxycyclohexane, and the heats of formation of 14 ethers (Table 4). These successful predictions imply that the additional parameters associated with non-bonded and torsional interactions involving oxygen atoms have been correctly assigned. The literature estimate [21] of the torsional barrier for the C–C bond in ethylene glycol

TABLE 3

Comparison of observed and calculated structural data

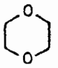
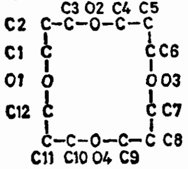
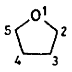
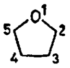
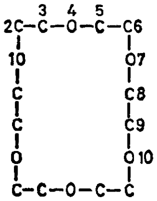
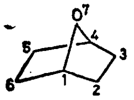
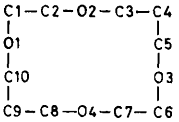
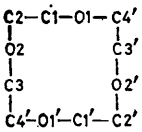
Compound		Obs.	Calc.	Calc. — obs.	Ref.
Dimethyl ether CH_3-O-CH_3	l_{C-H}	1.094 ± 0.006	1.101	0.007	*a*
	l_{C-O}	1.416 ± 0.003	1.416	0.000	
	θ_{C-O-C}	111.5 ± 1.5	112.0	0.5	
	C · · · C	2.342 ± 0.010	2.348	0.006	
	O · · · H	2.060 ± 0.010	2.059	−0.001	
	C · · · H	2.59, 3.29	2.63, 3.30	0.04, 0.01	
	H · · · H	1.78	1.79	0.01	
Methyl ethyl ether $CH_3-O-CH_2CH_3$ *trans*	$l_{O-C(Me)}$	1.415	1.416	0.001	*b*
	$l_{O-C(Et)}$	1.425	1.416	−0.009	
	θ_{C-C-O}	108.88	108.79	−0.09	
	θ_{C-O-C}	112.58	112.04	−0.54	
Diethyl ether $CH_3CH_2-O-CH_2CH_3$ *trans*; *trans*	l_{C-O}	1.433	1.417	−0.016	*c*
	l_{C-C}	1.512	1.522	0.010	
	θ_{C-O-C}	111.65	112.02	0.37	
	θ_{C-C-O}	107.54	108.88	1.34	
Tetrahydropyran  Chair (C_s)	l_{C-H}	1.116	1.101	−0.015	*d*
	l_{C-O}	1.420	1.422	0.002	
	l_{C-C}	1.531	1.528	−0.003	
	θ_{H-C-H}	110.1(9)	108.7	−1.4	
	θ_{C-O-C}	111.5(9)	112.9	1.4	
	$\theta_{C-C-C-(C)}$	108.3(15)	109.8	1.5	
	θ_{O-C-C}	111.8(3)	110.5	−1.3	
	$\theta_{C-C-C-(O)}$	110.9(12)	110.2	−0.7	
	$\omega_{O-C-C-C}$	56.9(6)	56.3	−0.6	
	$\omega_{C-C-C-C}$	52.5(12)	53.0	0.5	
	$\omega_{C-O-C-C}$	59.9(12)	61.6	1.7	
1, 4 - Dioxan  Chair (C_{2h})	l_{C-C}	1.523	1.528	0.005	*e*
	l_{C-O}	1.423	1.420	−0.003	
	θ_{C-O-C}	112.5	112.1	−0.4	
	θ_{O-C-C}	109.2	109.4	0.2	
	Av. ring angle	110.3	110.3	0.0	
	Av. torsion angle	57.9	57.9	0.0	
Oxetan  Planar	l_{C-H}	1.08	1.10	0.02	*f*
	l_{C-C}	1.54 ± 0.03	1.52	−0.02	
	l_{C-O}	1.46 ± 0.03	1.41	−0.05	
	θ_{C-C-C}	88.5 ± 3°	87.3	−1.2	
	θ_{C-O-C}	94.5 ± 3°	95.9	1.4	
	Ring torsion angles		0.0		
1,5,9,13-Tetraoxacyclohexadecane  Square conformation (D_{2d})	$\langle l_{C-O}\rangle$	1.415(5)	1.418	0.003	*g*
	$\langle l_{C-C}\rangle$	1.507(6) *	1.528	(0.021)	
	θ_{C-C-C}	112.9(4)	112.9	0.0	
	θ_{C-O-C}	113.3(4)	112.0	−1.3	
	θ_{C-C-O}	108.3(4)	110.1	1.8	
	ω(O1–C1)	171.0	175.5	4.5	
	ω(C1–C2)	−65.0	−62.4	2.6	
	ω(C2–C3)	−64.3	−61.8	2.5	
	ω(C3–O2)	175.1	176.8	1.7	
	ω(O2–C4)	−173.6	−175.0	−1.4	
	ω(C4–C5)	65.8	61.8	−4.0	
	ω(C5–C6)	62.8	61.2	−1.6	
	ω(C6–O3)	−171.2	−176.3	−5.1	

TABLE 3 (*Continued*)

	Compound	Obs.	Calc.	Calc. − obs.	Ref.
Tetrahydrofuran  Half-chair (C_2)	l_{C-O}	1.43 ± 0.03	1.42	−0.01	*h*
	l_{C-C}	1.54 ± 0.02	1.52	−0.02	
	θ_{C-O-C}	110.5	109.3	−1.2	
	θ_{C-C-O}	106.5	105.9	−0.6	
	θ_{C-C-C}	101.8	100.4	−1.4	
	ω(12)	11.6	13.6	2.0	
	ω(23)	29.6	34.8	5.2	
	ω(34)	35.0	41.0	6.0	
Tetrahydrofuran  Envelope (C_s)	θ_{C-O-C}	106.2	105.8	−0.4	*i*
	θ_{C-C-O}	105.0	103.7	−1.3	
	θ_{C-C-C}	104.0	103.9	−0.1	
	ω(12)	39.2	43.0	3.8	
	ω(23)	23.0	25.1	2.1	
	ω(34)	0	0.1	0.1	
18-Crown-6  Conformation (3c) (C_i)	l_{C-C}	1.507 *	1.523	(0.016)	*j*
	l_{C-O}	1.410	1.417	0.007	
	θ_{C-O-C}	113.5	113.2	−0.3	
	θ_{O-C-C}	109.8	109.1	−0.7	
	ω(O1–C2)	−79.7	−77.2	2.5	
	ω(C2–C3)	75.4	69.1	6.3	
	ω(C3–O4)	−155.2	−176.6	−21.4	
	ω(O4–C5)	165.8	173.1	7.3	
	ω(C5–C6)	−67.6	−61.6	6.0	
	ω(C6–O7)	175.5	171.8	3.7	
	ω(O7–C8)	174.7	179.7	5.0	
	ω(C8–C9)	174.7	177.1	2.4	
	ω(C9–O10)	170.1	178.9	8.8	
7-Oxanorbornane  (C_s)	l				
	$_{C_2-C_3}$	1.517	1.525	0.008	*k*
	$l_{C_1-C_2}$	1.533	1.527	−0.006	
	$l_{C_1-O_7}$	1.442	1.413	−0.029	
	θ_{C-O-C}	94.5	98.2	3.7	
	ω_{2145}	113.5	115.0	1.5	
1,4,8,11-Tetraoxacyclotetradecane  Conformation (4a) (C_2av)	l_{C-O}	1.426	1.418	−0.008	*l*
	l_{C-C}	1.509 *	1.526	(0.017)	
	$\theta_{C_{10}-O_1-C_1}$	114.0	113.4	−0.6	
	$\theta_{O_1-C_1-C_2}$	113.0	111.4	−1.6	
	$\theta_{C_1-C_2-O_2}$	109.8	110.4	0.6	
	$\theta_{C_2-O_2-C_3}$	112.1	112.2	0.1	
	$\theta_{O_2-C_3-C_4}$	108.4	109.7	1.3	
	$\theta_{C_3-C_4-C_5}$	112.8	112.9	0.1	
	$\theta_{C_4-C_5-C_3}$	107.6	109.6	2.0	
	ω(O1–C1)	−90.9	−88.3	2.6	
	ω(C1–C2)	76.5	66.8	−9.7	
	ω(C2–O2)	−172.1	−176.6	−4.5	
	ω(O2–C3)	178.0	−178.6	3.4	
	ω(C3–C4)	−64.4	−64.3	0.1	
	ω(C4–C5)	−70.0	−65.5	4.5	
	ω(C5–O3)	168.4	170.9	−2.5	
1,4,7,10-Tetraoxacyclododecane  Conformation (2f) (C_i)	$l_{O_1-C_1}$	1.430	1.418	−0.012	*m*
	$l_{O_2-C_2}$	1.429	1.418	−0.011	
	$l_{C_1-C_2}$	1.502 *	1.524	(0.022)	
	$\theta_{O_1-C_1-C_2}$	110.3	110.3	0.0	
	$\theta_{O_2-C_2-C_1}$	111.9	109.2	−2.7	
	$\theta_{O_2-C_3-C_4}$	108.5	107.6	−0.9	
	$\theta_{C_1-O_1-C_4'}$	113.1	112.7	−0.4	
	$\theta_{C_2-O_2-C_3}$	114.1	113.9	−0.2	
	$\theta_{C_3-C_4-O_1'}$	112.3	109.1	−3.2	
	ω(O1–C1)	140.2	152.2	12.0	
	ω(O2–C2)	102.7	103.4	0.7	
	ω(C3–O2)	−173.6	−167.9	5.7	
	ω(C1–C2)	−75.4	−70.7	4.7	
	ω(C3–C4)	74.5	68.9	−5.6	
	ω(C4–O1′)	85.2	96.4	11.2	

* Shortening of the C–C bond is an artificial effect arising from inadequate treatment of curvilinear vibrations in the crystal structure analysis.

[a] K. Kimura and M. Kubo, *J. Chem. Phys.*, 1959, **30**, 151. [b] L. Pierce and M. Hayashi, *Spectrochim. Acta*, 1962, **18**, 1370. [c] D. Andre, R. Fourme, and K. Zechmeister, *Acta Cryst.*, 1972, **B28**, 2389. [d] H. E. Breed, G. Gundersen, and R. Seip, *Acta Chem. Scand.*, 1979, **A33**, 225. [e] M. Davis and O. Hassel, *Acta Chem. Scand.*, 1963, **17**, 1181. [f] Personal communication quoted by W. Shand in 'Tables of Interatomic Distances and Configuration in Molecules and Ions,' The Chemical Society, London, 1958, p. 151. [g] P. Groth, *Acta Chem. Scand.*, 1971, **25**, 725. [h] D. Cremer and J. A. Pople, *J. Amer. Chem. Soc.*, 1975, **97**, 1358; H. J. Geise, W. J. Adams, and L. S. Bartell, *Tetrahedron*, 1969, **25**, 3045. [i] A. Almenningen and H. M. Seip, *Acta Chem. Scand.*, 1969, **23**. 2748. [j] Ref. 34. [k] K. Oyanagi, T. Fukuyama, K. Kochitsu, R. K. Bohn, and S. Li, *Bull. Chem. Soc. Japan*, 1975, **48**, 751. [l] Ref. 39. [m] Ref. 27.

TABLE 4

Comparison of experimental and calculated heats of formation for ethers, ΔH_f^0 (gas; 25 °C)/kcal mol^{-1}

Ether	E_s	ΔH_f^0(gas), obs.[a]	ΔH_f^0(gas), calc.	Calc. − obs.[b]
Dimethyl	0.82	-43.99 ± 0.12	−44.46	−0.47
Diethyl	0.77	-60.26 ± 0.19	−59.46	0.80
Di-n-propyl	0.85	-69.85 ± 0.40	−70.40	−0.55
Di-n-butyl	1.10	-79.82 ± 0.27	−81.17	−1.35
Methyl ethyl	0.83	-51.72 ± 0.16	−51.93	−0.21
Methyl propyl	0.88	-56.82 ± 0.26	−57.39	−0.57
Di-t-butyl	11.09	-87.10 ± 0.40	−87.99	−0.89
Methyl t-butyl	4.25	-69.7 ± 1.3	−67.93	1.77
Methyl isopropyl	2.18	-60.24 ± 0.23	−60.28	−0.04
Di-isopropyl	3.46	-76.20 ± 0.54	−76.18	0.02
Tetrahydropyran	4.02	-53.39 ± 0.24	−52.12	1.27
Tetrahydrofuran	9.38	-44.02 ± 0.17	−41.25	2.77
Oxetan	27.54	-19.25 ± 0.15	−19.25	0.00
1,4-Dioxan	2.45	-75.51 ± 0.17	−76.78	−1.27

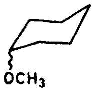
[a] All experimental heats of formation taken from J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometalic Compounds,' Academic Press, New York, 1970. [b] Mean deviation 0.86 kcal mol^{-1}

TABLE 5

Comparison of observed and calculated conformational properties of ethers

A Energy barriers in some ethers	Obs.	Calc.	Ref.
Ring inversion barrier in 1,4-dioxan	9.7	9.2	*a, b*
Ring inversion barrier in tetrahydropyran	9.3 (CD_3OD)	9.7	*c*
	9.9 (CS_2)		*d*
Energy barrier in dimethyl ether	2.72	2.69	*e*

B Conformational energies of some ethers[e]

Compound (conformations)	Favoured ΔG (obs.)	ΔH (obs.)	ΔH (calc.) (ref. 13)	ΔH (calc.) (this work)
1 $C_2H_5OC_2H_5$ (*t,t*; *t,g*)	*t,t*	1.1	0.84	1.27
2  (equatorial and axial)	Equatorial 0.45		0.33	0.46
3  (Half-chair and envelope)	Same 0 ± 0.3		0.36 (Half-chair)	0.50 (Half-chair)
4 	Planar		Planar	Planar

C Summary of ether conformations * from i.r. studies[f]

	Observed conformations			
Ether	Liquid (*ca.* 25 °C)	Annealed solid (−196 °C)	Calculated conformational energies	
Methyl Ethyl	*t* and *g*	*t*	E_s of *t*	0.83
	(*t* > *g*)		*g*	2.12
Diethyl	*tt* and *tg*	*tt*	E_s of *tt*	0.77
	(*tt* > *tg*)		*tg*	2.04
			gg	3.44
1,2-Dimethoxyethane	*tgt* and *ttt*	*tgt*	E_s of *tgt*	0.57
	and others		*ttt*	0.13
			tg^+g^-	1.84
			tg^+g^+	1.82
Methyl isopropyl	C_1 and C_s	C_1	E_s of C_1	2.18
	($C_1 \gg C_s$)		C_s	3.84
Ethyl isopropyl	C_1 (a) and C_1 (b)	C_1 (a)	E_s of C_1 (a)	2.02
	C_1 (a) $\gg$ C_1 (b)		C_1 (b)	3.53
			C_s	3.66
2,5-Dimethyldioxan		C_i (ee)	E_s of C_i (ee)	1.98
			C_i (aa)	5.17

* *t* = *trans*; *g* = *gauche*, E_s = steric energy. All energies in kcal mol^{-1}.

[a] F. A. L. Anet and J. Sandstrom, *Chem. Comm.*, 1971, 1558. [b] F. R. Jensen and R. A. Neese, *J. Amer. Chem. Soc.*, 1971, **93**, 6329. [c] J. D. Lambert and R. G. Keske, *J. Org. Chem.*, 1966, **31**, 3429. [d] G. Gatti, A. L. Segre, and C. Morandi, *J. Chem. Soc.* (*B*), 1967, 1203. [e] Ref. 13. [f] R. G. Snyder and G. Zerbi, *Spectrochim. Acta*, 1967, **23A**, 391.

appears to be unreasonably high: the value that we calculate (3.7 kcal mol^{-1}) is of reasonable magnitude and consistent with other experimental data.

Calculations for Crown Ethers.—Cyclic oligomers containing the oxyethylene unit have not yet been examined by MM calculations in spite of the high current level of interest in their properties. The newly developed ether force field was used to examine the systems * which are experimentally best defined,[22] including 1,4,7-trioxacyclononane (9-crown-3), 1,4,7,10-tetraoxacyclododecane (12-crown-4), and 1,4,7,10,13,16-hexaoxacyclo-octadecane (18-crown-6). In addition 1,4,8,11-tetraoxacyclotetradecane was also examined.

TABLE 6

Group enthalpy increments (kcal mol^{-1})

Group	Increment	E.s.d.
$-O-(CH_3)$	−12.33	0.10
$-O-(CH_2)$	−14.30	0.03
$-O-(CH_2)_{strain}$	−15.13	0.25
$-O-(CH)$	−16.91	0.21
$-O-(C)$	−17.73	0.13

TABLE 7

Calculated ring torsion angles and steric energy components for the transition states in the inversion of cyclohexane, tetrahydropyran, and 1,4-dioxan. The transition states were generated using the mapping method of K. B. Wiberg and R. H.Boyd (*J. Amer. Chem. Soc.*, 1972, **94**, 8426), with the minimal number of constraints [7] and were checked by the Newton–Raphson maximisation procedure (O. Ermer, *Tetrahedron*, 1975, **31**, 1849)

Compound	ω_{6123}	ω_{1234}	ω_{2345}	ω_{3456}	ω_{4561}	ω_{5612}	E_l [a]	E_θ [a]	E_r [a]	E_ω [a]	E_Q [a]	E_s [a]
Cyclohexane	21.7	−5.5	21.7	−53.3	69.2	−53.3	0.27	2.40	3.57	7.48	0.00	13.72
Tetrahydropyran	−44.6	8.8	−3.4	30.3	−63.9	72.6	0.24	2.20	3.70	7.56	0.00	13.70
1,4-Dioxan	−26.0	8.0	−26.0	57.7	−73.7	57.7	0.22	3.13	3.81	6.17	−1.73	11.60

[a] $E_l = \sum_l 1/2k_l(l - l_0)^2$, $E_\theta = \sum_\theta 1/2k_\theta(\Delta\theta^2 - k_\theta^1\Delta\theta^3)$, $E_r = \sum_r \varepsilon\{-2/\alpha^6 + \exp[12(1 - \alpha)]\}$, $E_\omega = \sum_\omega 1/2k_\omega(1 + s \cos n \omega)$, $E_Q = \sum_{ij} q_iq_j(Dr_{ij})^{-1}$. For explanation of symbols, see Appendix. The E_s for the minimum energy conformations of tetrahydropyran and 1,4 dioxan are given in Table 4 and the E_s of cyclohexane is calculated to be 3.52 kcal mol^{-1} using WBFF2.

9-*Crown*-3 (1). The geometries and the steric energies of six conformations of 9-crown-3 (1a—f) were calculated. The conformations examined included the [333] conformation (1a), the [12222] conformation (1b), the three [234] conformations (1c—e), and the [9] conformation (1f). The results of these calculations are shown in Figure 1. The minimum energy conformation is calculated to be the [12222] conformation (1b) mainly as a result of its low torsional strain energy. Conformations (1f, a, and c) are calculated to be 0.83, 1.50, and 4.76 kcal mol^{-1} higher in enthalpy respectively than conformation (1b), all three having high torsional strain about C–O bonds. Conformations (1d and e) also exhibit high torsional strain but in addition they show the repulsive transannular interactions between the ring atoms and between the hydrogen atoms that are characteristic of many of the conformations of medium sized rings. For example, in conformation (1e) the O(5)–C(9) and C(1)–C(4) non-bonded distances are 2.73 and 2.87 Å, respectively. On the basis of our calculations, therefore, we predict that an equilibrium mixture of 9-crown-3 (1) would consist mainly of the conformations (1b and f) with small amounts of conformation (1a).

I.r. spectrometry indicates that 9-crown-3 adopts a single asymmetrical conformation in solution and in the solid state.[23,24] The ^{13}C n.m.r. spectrum, at low temperatures, is consistent with the presence of a single conformation having six non-equivalent carbon atoms. This conformation could be any of the conformations (1b—f) although a [234] conformation was preferred on the basis of site exchange processes observable in the ^{13}C n.m.r. spectrum.[24] These site exchanges are, however, also consistent [25] with the [9] conformation (1f).

12-*Crown*-4 (2). MM calculations were carried out for the six conformations (2a—f) of 12-crown-4 shown in Figure 2. The ' square ' or [3333] conformation (2a) was found to represent the global minimum energy conformation, the other five conformations (2b—f) being at least 1.8 kcal mol^{-1} higher in energy as a result of higher angle and torsional strain.

The conformation of 12-crown-4 has been investigated [26] by i.r. spectroscopy and ^{13}C n.m.r. and it was shown that it probably adopted the ' square ' conformation (2a), having the ether oxygens in ' side ' positions rather than ' corner ' positions, with four identical *gauche,gauche,anti*-conformations for the individual O–C–C–O unit. In the crystal structure, however, 12-crown-4 adopts [27] the [66] conformation (2f), which is calculated (Figure 2) to be 2.9 kcal mol^{-1} higher in energy than the [3333] conformation (2a) largely as a result of high torsional strain. It is worth noting that throughout the development of the ether force field conformation (2a) was consistently the lowest energy conformation. Conformation (2f), as found in the crystal structure, is close to a local minimum in the energy surface (see comparison in Table 3).

18-*Crown*-6 (3). Of the very large number of possible conformations of 18-crown-6 five (3a—e) were selected for study on the basis of available crystal structure data. Conformation (3a) is analogous to the conformation adopted by the corresponding hydrocarbon, cyclo-octadecane, in the crystalline state.[28] Conformation (3b)

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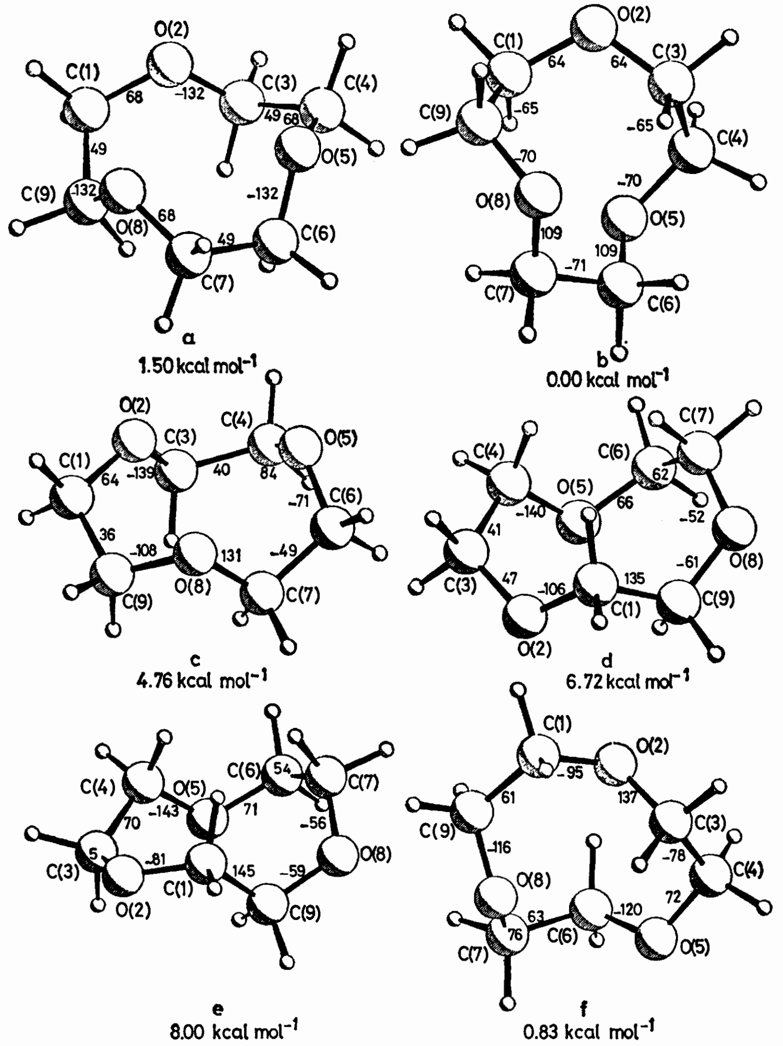
* The conformations examined are those that have been suggested in literature discussions or by experimental results.[22,23] The conformational descriptions [333] *etc.* are those used by Dale [23] and refer to the number of bonds in sides of the conformation containing a sequence of antiperiplanar bonds. Large numbers of conformational possibilities exist for macrocyclic compounds and it has not been possible to examine all possible conformations systematically.

is the conformation that the host macrocycle assumes in complexes with potassium thiocyanate,[29] rubidium thiocyanate,[30] caesium thiocyanate,[31] calcium thiocyanate,[32] ammonium bromide,[33] and benzylammonium thiocyanate (see below). Conformation (3c) corresponds to the conformation adopted by the free macrocycle in the crystalline state,[34] and conformations (3d and e) have been found for the eighteen-membered ring in the complexes of 18-crown-6 with sodium thiocyanate [35] and benzenesulphonamide,[36] respectively.



a 1.50 kcal mol^{-1}

b 0.00 kcal mol^{-1}

c 4.76 kcal mol^{-1}

d 6.72 kcal mol^{-1}

e 8.00 kcal mol^{-1}

f 0.83 kcal mol^{-1}

FIGURE 1 9-Crown-3 conformations; peripheral values are torsion angles and values below structures give steric energy (kcal mol^{-1}) relative to that of the minimum energy conformation

Conformation (3c) is found to be the minimum energy conformation, in accord with the experimental evidence,[34] furthermore the calculated geometry of this conformation is in reasonable agreement with the geometry found in the crystal structure (Table 3). The only major discrepancy is the C(3)–O(4) torsion angle and this is possibly the result of crystal packing forces, the calculated torsion angle (−176.6°) being very much closer to the minimum energy value (180°) than the torsion angle found in the crystal (−155.2°). Conformation (3c) is found to be more stable than the second lowest energy conformation (3a) by 3.86 kcal mol^{-1}, largely because the dipoles in the former conformation are aligned more favourably so that they give rise to more attractive electrostatic interactions. In addition conformation (3c) has only two of the less favourable gauche C–O torsion angles unlike conformation (3a) which has four. Conformation (3b),* although it is found in many cation

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* The calculated values of torsion angles in conformation (3b) are close to those of the expected minimum energy, symmetrical structure. The minor variations in calculated torsion angles for the antiperiplanar bonds indicate failure to obtain complete convergence in the molecular mechanics calculations. In general calculations were terminated when the root mean square of first derivatives of steric energy with respect to the co-ordinates was <0.02 kcal mol^{-1} Å^{-1} in the block-diagonal stage of the calculations and when the first derivatives of steric energy with respect to the co-ordinates were at least 10^{-3} kcal mol^{-1} Å^{-1} in the full-matrix stage of the calculations. This was to avoid waste of computing time.

complexes, has a relatively high steric energy being 7.84 kcal mol^{-1} less stable than conformation (3c). This is a consequence of the unfavourable alignment of dipoles in conformation (3b) together with the non-bonded O–O distances of 2.82 Å; indeed if it were not for these unfavourable electrostatic interactions conformation (3b) would be the lowest in energy of the five studied by 1.76 kcal mol^{-1}. This result is in satisfying agreement with the tendency of 18-crown-6 to adopt conformation (3b) in complexes with cations, when presumably the unfavourable electrostatic interactions between the oxygens are more than compensated by the favourable interactions between the oxygen atoms and the cationic centre. In complexes with ammonium salts the conformation (3b) is, of course, ideal for the formation of three hydrogen bonds between the ether oxygens and the $\overset{+}{N}H_3$ group of the ammonium salt (see below and ref. 33).

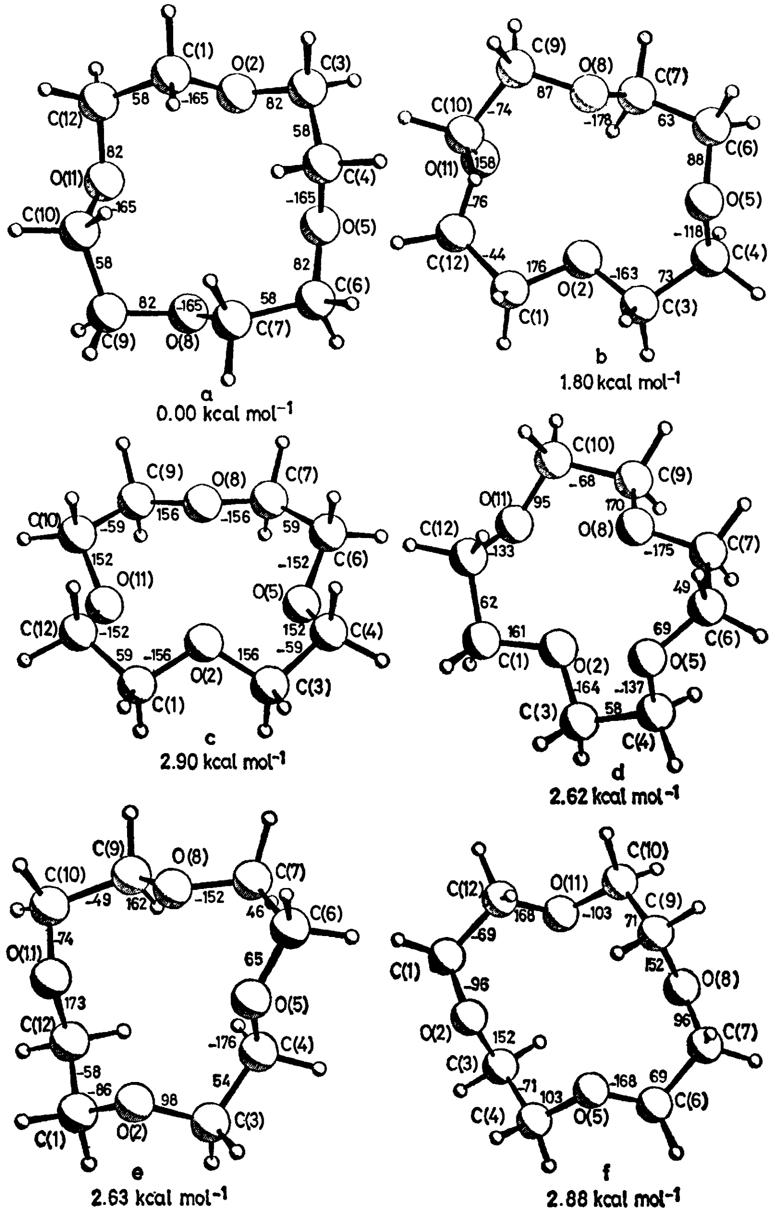
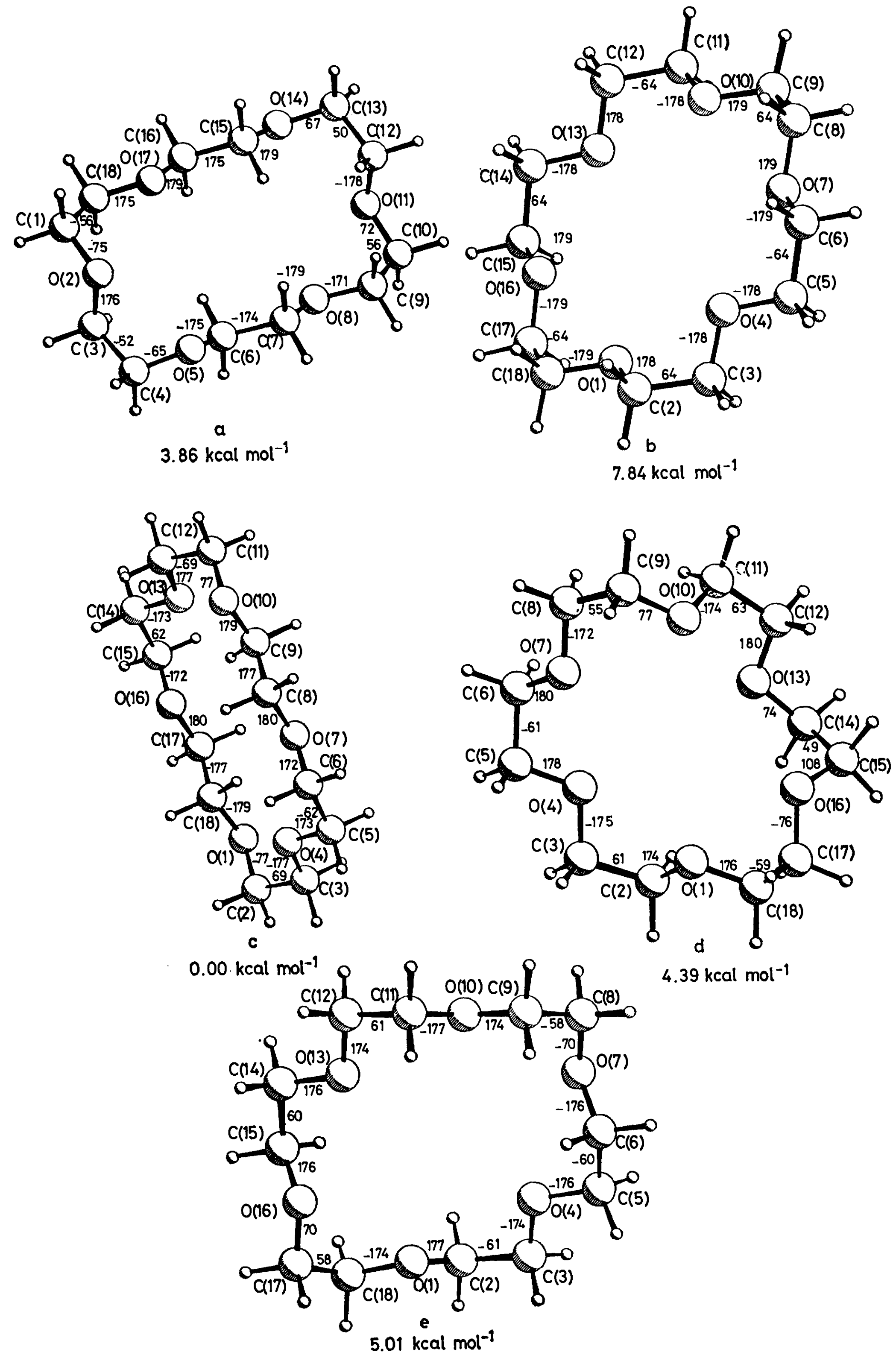


FIGURE 2 12-Crown-4 conformations

The conformation (3d), based upon that found in the sodium complex, has a highly irregular geometry although a large part of the macrocycle has torsion angles similar to those found in (3b). The strain in (3d) is largely associated with the C(15)–O(16) torsion angle (calculated value 107.7°); this results in torsional strain and the overcrowding of atoms in this part of the macrocycle [non-bonded distances include C(15)–C(18) 3.09, H(122)–H(152) 2.23, H(141)–H(181) 2.24, H(151)–H(171) 2.24, C(17)–H(151) 2.46 Å] together with opening of the



a
3.86 kcal mol^{-1}

b
7.84 kcal mol^{-1}

c
0.00 kcal mol^{-1}

d
4.39 kcal mol^{-1}

e
5.01 kcal mol^{-1}

FIGURE 3 18-Crown-6 conformations

C(17)–O(16)–C(15) bond angle to 114.9° to minimise the transannular interactions. Conformation (3e) has two pairs of consecutive gauche torsion angles which lead to serious transannular H–H overcrowding [non-bonded distances include H(61)–H(91) and H(152)–H(182) 2.20 Å].

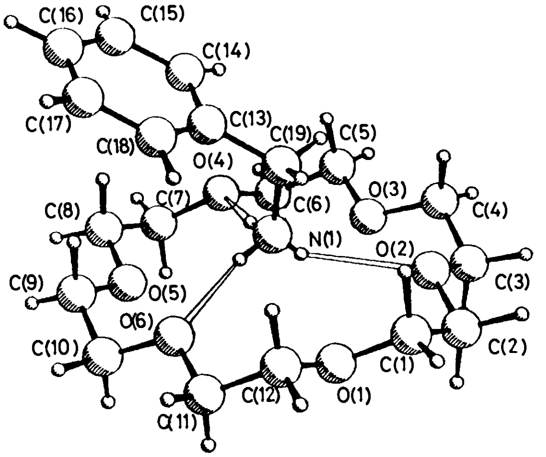


FIGURE 4 The molecular structure of the benzylammonium thiocyanate complex of 18-crown-6

The recognition that none of the fully characterised complexes of 18-crown-6 involve the minimum energy conformation of the macrocycle underlines the necessity for considering the complexing ability of host molecules in terms of the structure of the complex rather than the minimum energy conformation of the host macrocycle. It must also throw serious doubts upon the value of conformational studies of biologically important molecules that neglect conformations other than the global minimum

X-*Ray Crystal Structure Analysis of Benzylammonium Thiocyanate Complex of* 18-*Crown*-6.—At the outset of this work there was no report in the literature of the structure analysis of a crystalline complex of 18-crown-6 with an alkylammonium salt. Since then, the structure of a complex of 18-crown-6 with ammonium bromide has been described but, in view of the central position of the 18-crown-6 ring system in current work on guest–host complexes, the determination of the structure of a complex of a typical primary alkylammonium salt was considered to be important.

Details of the structure determination are given in the Experimental section, the molecular structure is shown in Figure 4, in projection onto the plane of the macrocycle in Figure 5, and the crystal structure is shown in Figure 6. Interatomic distances and angles are shown in Figure 7, and torsion angles in Figure 8.

The macrocycle conformation is similar to that observed in the corresponding potassium,[29] rubidium,[30] and caesium [31] thiocyanate complexes and the hydrated ammonium bromide complex,[33] having approximate D_{3d} symmetry. The conformation about C–C bonds is synclinal (average torsion angle 68°; *cf.* 68° in the ammonium ion complex [33]) and about C–O bonds is antiperiplanar (average torsion angle 176°; *cf.* 175° in the ammonium ion complex [33]). The C–C–O bond angles are close to the tetrahedral value (average 109.3°), the C–O–C angles are somewhat bigger (average 113.0°).

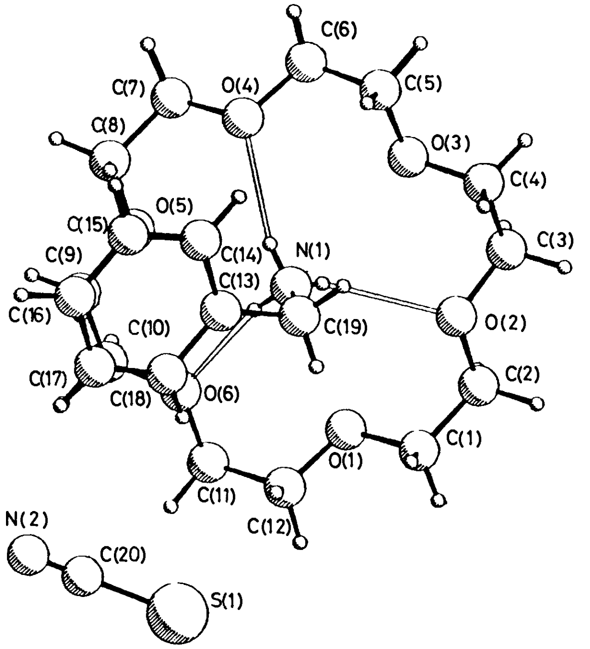


FIGURE 5 $C_7H_7NH_3{}^+NCS^-$, complex of 18-crown-6 viewed in a direction approximately normal to the mean plane through the six oxygen atoms of the macrocycle

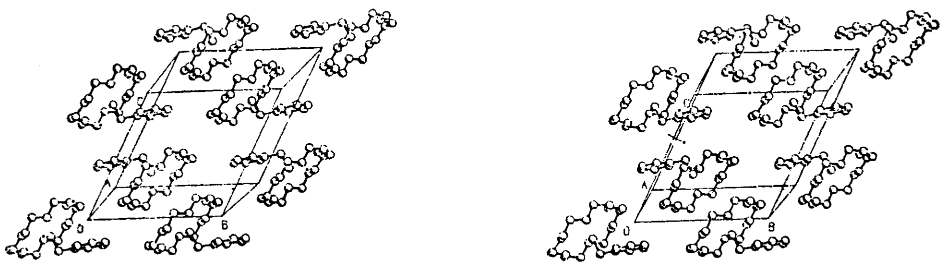


FIGURE 6 A stereoscopic view of the crystal structure of the benzylammonium thiocyanate complex of 18-crown-6

The benzylammonium cation forms three hydrogen bonds to oxygen atoms 2, 4, and 6 (Figures 4 and 5) [N(1) · · · O(2) 2.885 (13), N(1) · · · O(4) 2.924 (10), N(1) ··· O(6) 2.833 (9) Å]. The remaining oxygen atoms also display short N ··· O contacts [N(1) ··· O(1) 3.039 (10), N(1) ··· O(3) 2.925 (9), N(1) ··· O(5) 2.997 (13) Å]. The average N ··· O separation is 2.934 Å (*cf.* 2.980 in the ammonium ion complex,[33] $K^+ \cdots O$ 2.805, $Rb^+ \cdots O$ 3.024, $Cs^+ \cdots O$ 3.146 Å in the potassium,[29] rubidium,[30] and caesium [31] thiocyanate complexes). N(1) is displaced 0.86 Å from the mean plane of the macrocycle oxygen atoms (*cf.* displacements of K^+ 0.00, NH_4^+ 1.00, Rb^+ 1.19, and Cs^+ 1.44 Å) which implies a ' size ' order $Cs^+ > Rb^+ > NH_4^+ > PhCH_2NH_3^+ > K^+ \simeq$ cavity. The structural evidence for stronger binding of the benzylammonium compared with the ammonium cation can be rationalized on the basis of the additional hydrogen bond ($\overset{+}{N}H \cdots Br^-$) in the latter complex leading to a reduction in the overall partial charge on nitrogen and hence of the strengths of the remaining hydrogen bonds. The macrocycle oxygen atoms are on average 0.21 Å alternately above and below the oxygen mean plane with the oxygen atoms on the same side of the plane as the guest salt involved in hydrogen bonding; maximum deviations from the plane are observed for atoms O(4), O(5), and O(6) which are in the region over which the benzene ring of the guest salt lies. The hydrogen-bonded N–H atoms subtend angles of 160 [H(201) ··· O(6)], 143 [H(202) ··· O(4)], and 146° [H(203) ··· O(2)] with the bisectors of the corresponding C–O–C angles in the C–O–C planes. This presumably reflects a compromise between the utilisation of lone pair electron density, requiring an angle of 125°, and the geometry imposed by the nature of the complex.* No interatomic contacts of <3.6 Å between the thiocyanate ion and non-hydrogen atoms were found. This lack of direct participation of the counter ion in complex formation is consistent with our earlier results obtained from a dynamic n.m.r. study [14] of guest–host binding. The conformation adopted by the macrocycle is remarkably close to that predicted for conformation (3b) by MM calculations. Conformation (3b) would be the minimum energy conformation for 18-crown-6 if it were not for the electrostatic repulsion between the oxygen atoms, but these electrostatic repulsions are presumably reduced in the complex. This is consistent with the remarkable ability of 18-crown-6 to form complexes with cations, the removal of unfavourable interactions in what would otherwise be a minimum energy conformation is a subtle way in which the complexing ability of a host molecule may be enhanced.

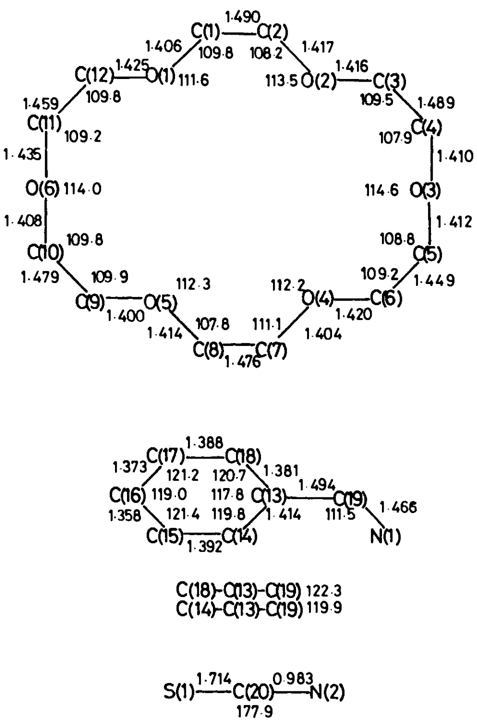


FIGURE 7 Interatomic distances and angles observed in the benzylammonium thiocyanate complex of 18-crown-6

1,4,8,11-*Tetraoxacyclotetradecane* (4) *and* 1,4,7,11-*Tetraoxacyclotetradecane* (5).—The conformational behaviour of 1,4,8,11-tetraoxacyclotetradecane has been studied by i.r. and n.m.r. spectroscopy [38] and *X*-ray crystallography.[39] Two conformations were studied by MM calculations, the non-diamond lattice [77] conformation (4a) and the diamond lattice [3434] conformation (4b) (Figure 9). Conformation (4a) was found to be more stable than conformation (4b) by 0.61 kcal mol^{-1} (Table 3). Although conformation (4a) has high torsional strain about the O(1)–C(2) and O(8)–C(9) bonds it has less angle strain and fewer repulsive transannular non-bonded H–H interactions than conformation (4b). Thus the H(3)–H(14) and H(7)–H(10) non-bonded distances in conformation (4b) are calculated to be 2.17 Å, well within the repulsive portion of the van der Waals curve for non-bonded H–H interactions. The shortest

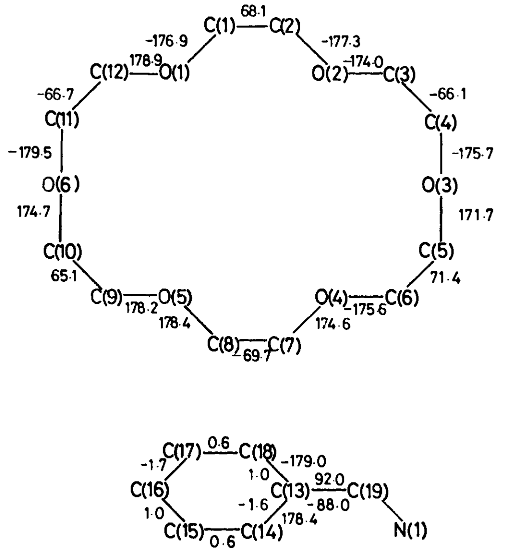


FIGURE 8 Torsion angles observed in the benzylammonium thiocyanate complex of 18-crown-6

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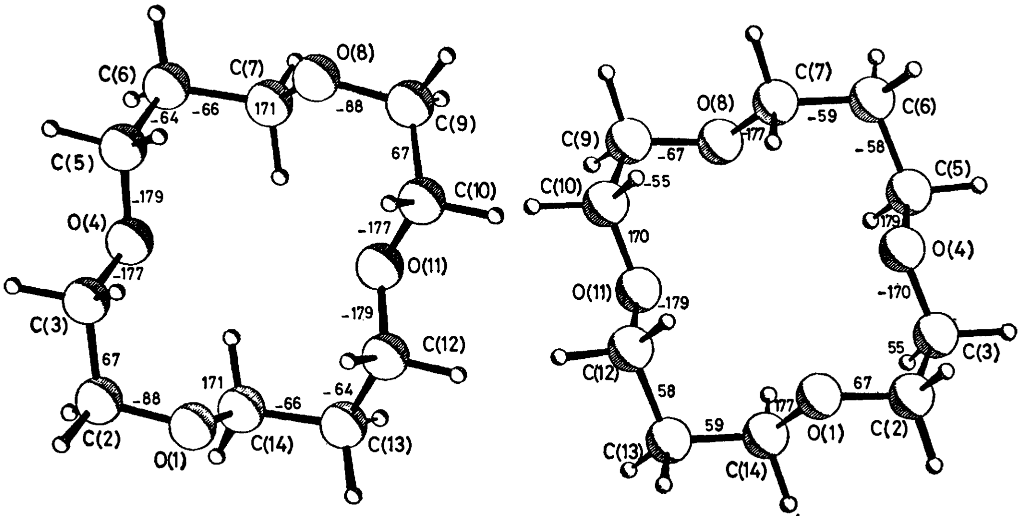
* For a discussion of the conformational requirements for complex formation by 18-crown-6 systems see ref. 37.

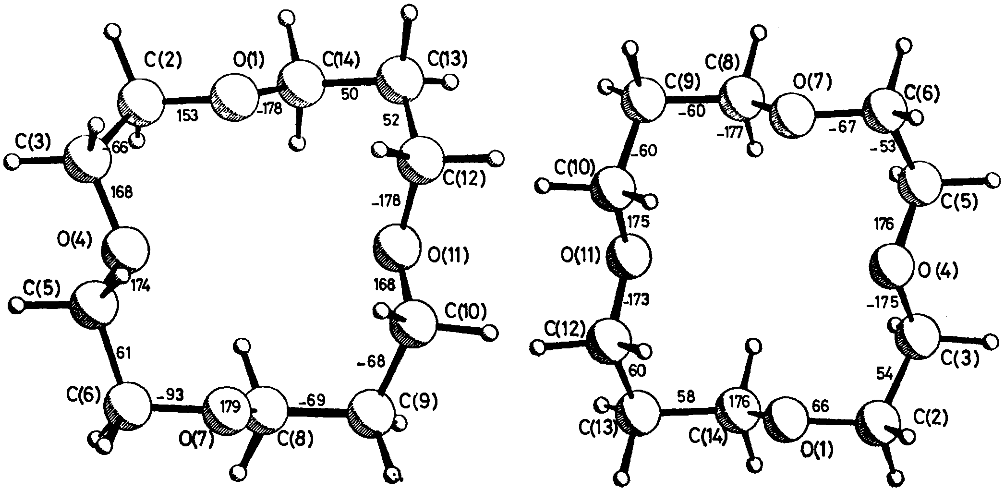
non-bonded distances in conformation (4a) are the O(4)–H(14) and O(11)–H(4) distances of 2.27 Å which is only slightly repulsive. The preferred conformation of the polyether (4) in the solid state,[39] the liquid state, and in CS_2 and CCl_4 solution [38] is the non-diamond lattice conformation (4a). However, in the polar solvent $CHCl_2F$ the diamond lattice conformation (4b) becomes increasingly populated as the temperature is lowered. The agreement between calculated and observed values for bond lengths, bond angles, and torsion angles for conformation (4a) is very satisfactory.



a
0.00 kcal mol⁻¹

b
0.61 kcal mol⁻¹

FIGURE 9 1,4,8,11-Tetraoxacyclotetradecane (4)



a
0.31 kcal mol⁻¹

b
0.00 kcal mol⁻¹

FIGURE 10 1,4,7,11-Tetraoxacyclotetradecane (5)

MM Calculations for the closely related macrocycle 1,4,7,11-tetraoxacyclotetradecane (5) show that the [410] conformation (5a) and the [3434] conformation (5b) (Figure 10), analogous to the two conformations (4a and b) discussed above, are closely similar in energy. In this case, however, the diamond lattice conformation (5b) is calculated to be the lower energy conformation by only 0.31 kcal mol⁻¹. The i.r. and n.m.r. spectra of (5) have been interpreted [38] in a similar way to those of its isomer (4). The non-diamond lattice [410] conformation (5a) is believed to be favoured in the liquid state and in CS_2 and CCl_4 solutions, but the diamond lattice [3434] conformation (5b) is increasingly favoured by polar solvents and low temperatures.

EXPERIMENTAL

Crystal and Molecular Structure of the Benzylammonium Thiocyanate Complex of 1,4,7,10,13,16-*Hexaoxacyclo-octadecane* (18-*Crown*-6).[*]—*Crystal data.* $C_{12}H_{24}O_6{\cdot}C_7H_7NH_3^+$-$NCS^-$, $M = 430.56$, triclinic, $P\bar{1}$, $a = 9.670(3)$, $b = 11.969(3)$, $c = 12.508(3)$ Å, $U = 1\,193.09$ Å^3, $\alpha = 63.17(2)$, $\beta = 65.98(2)$, $\gamma = 74.24(2)$, $Z = 2$, $D_c = 1.22$ g cm^{-3}.

Diffraction intensities from a crystal *ca.* 0.3 mm edges were measured on an Enraf–Nonius CAD 4 diffractometer with graphite-monochromatized Mo-K_α radiation. 1 349 Reflexions [1 231 with $I \geqslant 3\sigma(I)$] ($2\theta < 50°$) were recorded. The structure was solved by direct methods (MULTAN 78) [40] and refined by block-diagonal least squares (*X*-Ray system) [41] with unit weights. At an intermediate stage of the refinement, hydrogen atom positions for the NH_3^+ group were located from a difference Fourier synthesis: these and calculated positions for the remaining hydrogen atoms were subsequently included. It proved possible to refine (with isotropic thermal parameters) positions of all hydrogen atoms except for those located on the macrocycle carbon atoms 4, 5, 7, 8,. 10, and 12. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final *R* was 0.054: extinction corrections were not required. Final positional parameters are listed in Tables 8 and 9. Structure factors and vibrational parameters are listed in Supplementary Publication No. SUP 22824 (19 pp.).[†]

TABLE 8

Atomic co-ordinates for C, O, N, S ($\times 10^4$)
(e.s.d.s in parentheses)

	x/*a*	*y*/*b*	*z*/*c*
S(1)	9 100(3)	8 034(3)	3 418(3)
O(1)	8 034(7)	12 722(6)	1 979(6)
N(1)	4 750(7)	12 562(6)	2 421(6)
O(2)	5 578(7)	13 992(6)	3 369(6)
O(5)	4 628(8)	12 517(6)	0 085(6)
O(4)	2 096(7)	13 663(6)	1 578(6)
C(18)	4 729(9)	9 485(8)	3 403(8)
O(6)	7 251(7)	11 547(6)	0 812(6)
C(14)	2 212(10)	10 567(8)	3 789(8)
C(13)	3 765(10)	10 507(7)	3 617(7)
C(15)	1 711(10)	9 630(9)	3 709(9)
O(3)	2 903(7)	14 845(6)	2 734(6)
C(16)	2 683(12)	8 643(9)	3 478(9)
C(17)	4 185(12)	8 562(8)	3 342(9)
N(2)	7 992(10)	7 151(10)	2 320(10)
C(19)	4 311(9)	11 529(7)	3 669(7)
C(8)	3 092(17)	12 496(15)	0 262(11)
C(7)	2 226(15)	13 668(15)	0 417(13)
C(5)	1 397(13)	14 791(11)	2 869(15)
C(3)	4 671(16)	15 131(10)	3 406(10)
C(2)	7 125(14)	13 991(12)	3 185(10)
C(4)	3 045(15)	14 993(11)	3 740(11)
C(1)	7 964(12)	12 773(11)	3 102(10)
C(20)	8 410(12)	7 486(10)	2 701(12)
C(10)	7 141(18)	11 518(12)	−0 264(11)
C(6)	1 389(14)	14 827(12)	1 698(16)
C(9)	5 544(19)	11 425(12)	−0 039(11)
C(12)	8 759(11)	11 543(10)	1 895(13)
C(11)	8 781(13)	11 522(11)	0 731(13)

APPENDIX

The steric energy E_S of a molecule is defined as the sum of the contributions from each of the terms describing potential energy as a function of molecular deformations from an arbitrary reference geometry [equation (2); *l*, θ, *r*, and ω are bond lengths, angles, 1,4 and higher interatomic distances, and torsion angles, respectively]. The improper torsion angle χ describes out-of-plane bending at the trigonal atoms.[42] The values of the force constants k_l, k_θ, $k_\theta{}^1$, k_ω, ε, and k_χ and the equilibrium geometric parameters l_0,

$$E_S = \sum_l \tfrac{1}{2}k_l(l - l_0)^2 + \sum_\theta \tfrac{1}{2}k_\theta(\Delta\theta^2 - h_\theta{}^1\Delta\theta^3) + \sum_\omega \tfrac{1}{2}k_\omega(1 + s\cos n\,\omega) + \sum_r \varepsilon\{-2/\alpha^6 + \exp[12(1 - \alpha)]\} + \sum_\chi \tfrac{1}{2}k_\chi(180 - \chi)^2$$

$$\alpha = r/(r_1{}^* + r_2{}^*);\quad \Delta\theta = \theta - \theta_0 \qquad (2)$$

θ_0, *s*, *n*, and *r** for alkanes and alkenes are given in Table 1, while those for ethers are given in Table 2.

TABLE 9

Atomic co-ordinates for H ($\times 10^4$)
(e.s.d.s of refined parameters in parentheses)

	x/*a*	*y*/*b*	*z*/*c*
H(41)	2 796	14 215	4 561
H(42)	2 405	15 738	3 914
H(51)	0 966	13 968	3 584
H(52)	0 633	15 499	3 099
H(71)	1 206	13 788	0 290
H(72)	2 828	14 377	−0 354
H(81)	2 580	11 798	1 098
H(82)	2 922	12 410	−0 434
H(101)	7 781	10 783	−0 487
H(102)	7 443	12 316	−1 051
H(121)	8 185	10 819	2 642
H(122)	9 837	11 374	1 915
H(11)	7 384(83)	11 897(67)	4 003(68)
H(12)	8 872(89)	12 600(72)	3 254(73)
H(21)	7 183(92)	14 103(77)	3 980(80)
H(22)	7 572(75)	14 777(62)	2 273(67)
H(31)	4 787(104)	15 296(86)	4 118(84)
H(32)	5 020(82)	15 963(69)	2 464(72)
H(61)	0 424(101)	15 014(80)	1 661(82)
H(62)	1 958(99)	15 638(79)	0 922(79)
H(91)	5 192(90)	10 581(75)	0 870(77)
H(92)	5 439(92)	11 350(77)	−0 688(81)
H(111)	9 350(81)	10 712(71)	0 718(69)
H(112)	9 243(91)	12 241(79)	−0 042(77)
H(191)	3 604(59)	11 934(48)	4 213(50)
H(192)	5 105(65)	11 225(52)	3 938(53)
H(201)	5 346(63)	12 271(50)	1 923(50)
H(202)	4 062(61)	12 755(48)	2 154(49)
H(203)	4 953(61)	13 077(49)	2 347(49)
H(18)	5 742(72)	9 552(60)	3 235(61)
H(17)	4 739(70)	7 887(58)	3 249(59)
H(16)	2 361(62)	7 943(52)	3 414(52)
H(15)	0 737(70)	9 783(59)	3 713(60)
H(14)	1 601(70)	11 327(57)	3 881(58)

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