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Spectroscopic and crystallographic study of 27,28-diethoxy-*p-tert*-butylcalix[4]arenes

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Abstract

$C_{48}H_{64}O_4$, M_r = 705.04, monoclinic, $P2_1/n$, a = 14.509(2) Å, b = 17.913(4) Å, c = 16.899(1) Å, β = 107.343(9)°, V = 4192.4(11) Å^3, Z = 4, D_x = 1.117 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ = 0.74 cm^{-1}, F(000) = 1536, T = 100 K, R = 0.059 for 5505 observed reflections with $I > 2.5\sigma(I)$.

The molecular conformation of the anti form of the title compound, i.e. with the two neighbouring phenylethylether fragments in anti positions, is a partial cone. The conformation is stabilized by two intramolecular hydrogen bonds. These bonds involve both the phenolic OH groups as donors and a hydroxyl group and an ethoxygroup as acceptors. FT-IR solid state spectra reveal two OH bands at 3388 and 3175 cm^{-1} which is in accordance with the observed hydrogen-bond configuration. In CCl_4 solution the partial cone is preserved for the anti form (3378 and 3187 cm^{-1}) while the corresponding syn form mainly adopts a cone conformation characterized by O–H stretching vibrations at 3360 and 3168 cm^{-1}.

INTRODUCTION

The phenol-formaldehyde cyclic oligomers, called calixarenes, form a class of phenolic macrocycles having methylene bridges at positions ortho to the phenolic OH groups. The X-ray structures of calixarenes having four [1], five [2], six [3], seven [4], or eight [5] phenolic units have been reported. Of particular interest are the calix[4]arenes since, depending on the degree

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of substitution of the OH groups (lower rim) and the presence of bulky para substituents (upper rim), like *p-tert*-butyl, the conformational flexibility of the macrocycles can be drastically influenced. Although O-unsubstituted calix[4]arenes are conformationally mobile in solution, their solid state structure is characterized by a four-membered ring of strong O–H···O hydrogen bonds which force the calix[4]arene into the so-called cone conformation. Substitution at the lower rim of the calix[4]arenes disrupts the circular hydrogen-bond system, allowing three additional conformations [6] (see Fig. 1). The first is the partial cone which can be derived from the cone by rotation of one phenol residue through the annulus of the molecule. So far only four X-ray structures of calix[4]arenes in the partial cone conformation have been reported [7–10]. The second type, the 1,2-alternate, arises from the cone by rotating two neighbouring phenol fragments. So far only three X-ray structures of this type are known [10–12]. The last is the 1,3-alternate, which originates from rotation of two opposite phenol rings. This type is also rare; only three X-ray structures [11–13] show this conformation.

Recently the crystal structures of two calix[4]arene alkylethers have been reported. One involves a mixed ether, *syn*-1,2-diethoxy-3,4-dimethoxy-*p-tert*-butylcalix[4]arene[a] which occurs in the partial cone conformation [10]. Interestingly, two conformations of the second one, *p-tert*-butylcalix[4]-arene tetraethylether, have been reported: a partial cone conformation [14] and the rare 1,2-alternate conformation [10].

In an earlier study the conformations of partially methylated *p-tert*-butylcalix[4]arene have been investigated by molecular mechanics, X-ray crystallography and ^{1}H NMR spectroscopy [7]. It was found that the mono-, di- and trimethylethers all exist preferentially in a cone conformation. However, no experimental data were reported for the 1,2-dimethylated calix[4]arene.

For the *anti*-1,2-diethylether, three conformations, partial cone, 1,2-alternate and 1,3-alternate, are formally possible. The phenolic OH groups will tend to establish intramolecular hydrogen bonds, which can only be realized in the partial cone and 1,2-alternate forms. These forms exhibit different hydrogen-bonding schemes: O–H···O–H···O–Et in the partial cone and two O–H···O–Et bonds in the 1,2-alternate form. Also the *syn*-1,2-diethylether can adopt three different conformations, namely the cone, the partial cone and the 1,2-alternate. Only in the cone can two hydrogen bonds be formed.

[a] In this paper we follow the proposal of Groenen et al. [10] for the nomenclature of substituted calix[4]arenes. The prefix *syn* indicates that two O-substituted substituents are on the same face of the molecule, whereas the prefix *anti* denotes that two O-substituted substituents are on different faces of the molecule.

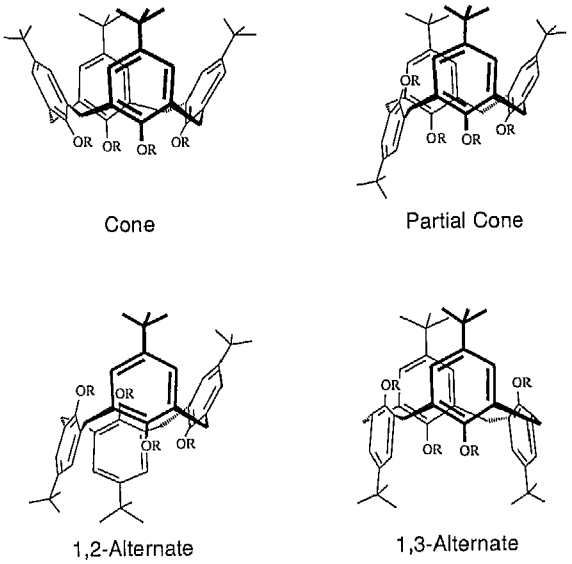

Fig. 1. Schematic drawing of the conformations of calix[4]arenes.

In order to study the balance of conformation-determining effects of these different hydrogen-bonding schemes in the solid state and in solution, we undertook the X-ray analysis and infrared spectroscopy of *anti*-1,2-diethoxy-*p-tert*-butylcalix[4]arene (ADET). In addition, the solution spectra of the title compound are compared with those of the corresponding *syn*-1,2-diethoxy-*p-tert*-butylcalix[4]arene (SDET).

EXPERIMENTAL

Materials

Crystals of ADET [10] suitable for X-ray analysis were grown from hexane. Crystals of SDET [15] of sufficient quality for X-ray analysis could not be obtained. All solvents used for the solution IR-measurements were of spectroscopic grade and were stored over molecular sieves.

X-ray measurements

A colourless crystal of ADET with dimensions $0.8 \times 0.4 \times 0.2\,mm^3$ was used for data collection on an Enraf–Nonius CAD-4 diffractometer with Zr-filtered Mo Kα radiation. Lattice parameters were determined from the setting angles of 25 reflections in the range $9.24° \leqslant \Theta \leqslant 19.23°$. The diffracted intensities of 9526 unique reflections were collected at liquid-nitrogen temperature (100 K) using the ω–2Θ scan mode, $\Delta\omega = (0.67 + 0.35 \tan\Theta)°$,

$2\Theta_{max} = 55°$ and $-18 \leqslant h \leqslant 18$, $0 \leqslant k \leqslant 23$, $-21 \leqslant l \leqslant 0$, of which 5505 with $I > 2.5\sigma(I)$ were considered observed. Three periodically measured standard reflections ($32\bar{5}$, 412 and $\bar{2}1\bar{3}$), measured every hour, showed an average deviation of less than 6% during 155 hours of X-ray exposure. Intensities were corrected for Lp effects, but not for absorption. The structure was solved in space group $P2_1/n$ by direct methods using SHELXS86 [16]. The hydroxyl H atoms were located from a different Fourier map and positionally refined. All other H atoms were introduced at calculated positions (C–H 1.00 Å) and refined with respect to their bonded atom, with an overall isotropic thermal parameter which refined to 0.0306(12) Å^2. Anisotropic full-matrix least-squares refinement on F of 476 parameters converged at $R = 0.059$ and $wR = 0.062$ with $w = 1.687/\sigma^2(F_0)$, $S = 1.73$, $(\Delta/\sigma)_{av} = 0.006$ and $(\Delta/\sigma)_{max} = 0.04$. Maximum and minimum residual densities in the final difference map are 0.43 and -0.36 eÅ^{-3}, respectively. The scattering factors were those of Cromer and Mann [17] and anomalous-dispersion terms from Cromer and Liberman [18]. The least-squares refinement was performed with the SHELX76 program [19] and the program package EUCLID [20] was used for the calculation of geometries and preparation of illustrations. All calculations were done on an ULTRIX DECsystem-5000.

FT-IR measurements

The FT-IR spectra were recorded on a Mattson 5020 connected to a PC at a resolution of 2 cm^{-1}. Solution spectra with a concentration less than 2 mg per 5 ml solvent were measured using 10 mm 'infrasil' cells. For the solid state spectra we used an RIIC-VLT-2 variable temperature unit equipped with KBr windows connected to a West M2071 microprocessor-based controller. Liquid nitrogen was used as coolant enabling us to obtain fluorolube mull spectra over a temperature range of 100–300 K. Second order derivative spectra were calculated on a PC using the standard Mattson First™ software.

RESULTS AND DISCUSSION

Crystal structure

The atomic coordinates together with equivalent isotropic thermal parameters (C and O atoms) are listed in Table 1. Bond distances and bond angles involving C and O atoms are given in Table 2[b]. A perspective view

[b] Non-hydrogen atom anisotropic thermal parameters, coordinates of the hydrogen atoms, and listings of observed and calculated structure factors are available as supplementary data (B.L.L.D. Supplementary Publication number SUP 26443 (61 pages)).

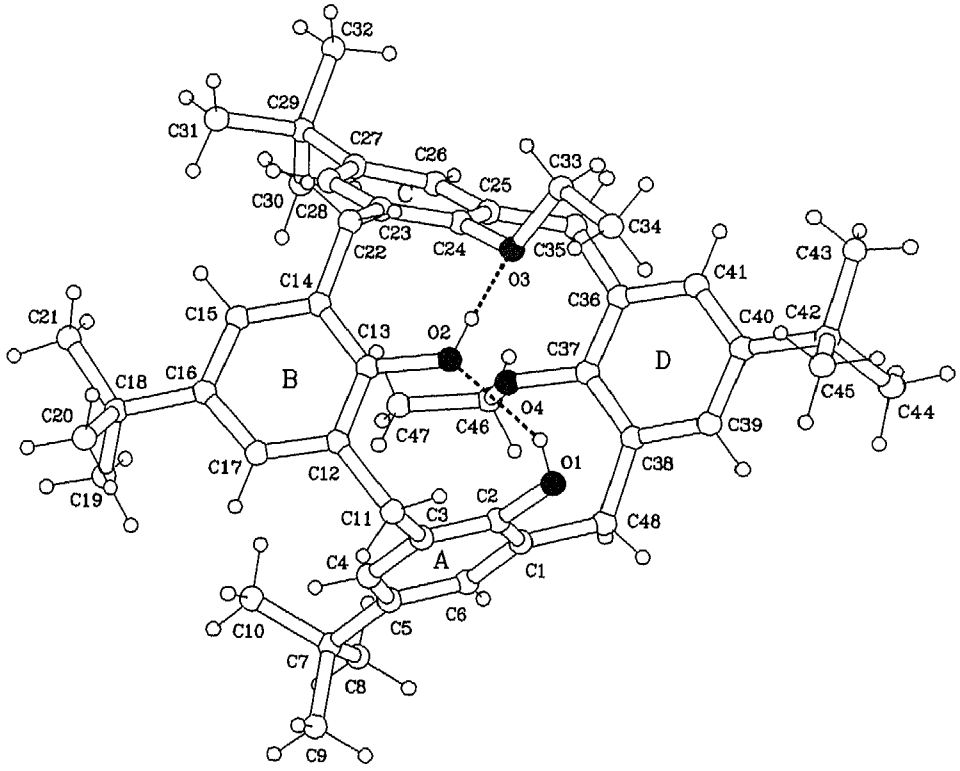

Fig. 2. Perspective view and atomic numbering of the title compound.

of the molecule with the adopted atom numbering scheme is shown in Fig. 2. As Fig. 2 shows, the phenyl ring D is rotated through the calixarene annulus which results in a partial cone conformation. Following the proposal of Groenen et al. [10], the title compound should be classified as an *anti*-diethoxy-calix[4]arene. In accordance with the partial cone conformation, the distances of the four O atoms to the plane of the four bridging methylene C atoms are: 1.299(9), 1.087(8), 1.170(8) and −1.101(8) Å, respectively. An elegant way to describe the exact conformation of calixarenes was recently proposed by Andreetti et al. [4]. This method circumvents the ambiguities inherent in the common use of the angles between the phenyl rings and the plane of the methylene carbon atoms. Instead the conformation is described by the torsion angles about the C–C bonds linking the phenyl rings. For a cone, the sequence of the eight torsion angles have alternate + and − signs. For a partial cone, i.e. when one of the phenyl rings is rotated through the annulus, the torsion angles should display the pattern + −, + −, + +, − − or the opposite. As shown in Table 3, the angles about the $C(sp^3)$–$C(sp^2)$ bonds uniquely define the conformation as

TABLE 1

Fractional coordinates and equivalent isotropic thermal parameters (Å^2) with esd values in parentheses

Atom	x	y	z	U_{eq}[a]
O(1)	0.84769(15)	0.27098(11)	0.43904(12)	0.0196(6)
O(2)	0.69852(14)	0.20374(11)	0.31190(12)	0.0180(6)
O(3)	0.55353(14)	0.27603(11)	0.33842(12)	0.0175(6)
O(4)	0.68676(14)	0.43053(11)	0.34569(11)	0.0183(6)
C(1)	0.89248(19)	0.39072(16)	0.40390(17)	0.0155(8)
C(2)	0.87911(18)	0.31527(15)	0.38575(17)	0.0154(8)
C(3)	0.89937(18)	0.28560(16)	0.31655(17)	0.0153(8)
C(4)	0.93272(18)	0.33264(15)	0.26627(17)	0.0153(8)
C(5)	0.94854(18)	0.40807(15)	0.28278(17)	0.0146(8)
C(6)	0.92822(19)	0.43623(15)	0.35293(17)	0.0155(8)
C(7)	0.9889(2)	0.45632(17)	0.22580(17)	0.0193(8)
C(8)	0.9892(2)	0.53894(17)	0.24677(19)	0.0251(9)
C(9)	1.0925(2)	0.43206(19)	0.2339(2)	0.0309(11)
C(10)	0.9265(3)	0.44636(19)	0.13499(19)	0.0317(10)
C(11)	0.88112(18)	0.20412(15)	0.29195(16)	0.0148(8)
C(12)	0.79077(19)	0.19925(15)	0.21869(17)	0.0149(8)
C(13)	0.70080(19)	0.20491(15)	0.23100(17)	0.0151(8)
C(14)	0.61709(19)	0.21090(15)	0.16364(17)	0.0161(8)
C(15)	0.6268(2)	0.21064(16)	0.08349(17)	0.0181(8)
C(16)	0.71615(19)	0.20426(16)	0.06952(17)	0.0166(8)
C(17)	0.79748(19)	0.19806(15)	0.13846(17)	0.0163(8)
C(18)	0.73016(19)	0.20594(17)	−0.01675(17)	0.0190(8)
C(19)	0.7967(2)	0.27082(19)	−0.02204(19)	0.0287(10)
C(20)	0.7756(2)	0.13251(19)	−0.03273(19)	0.0289(10)
C(21)	0.6346(2)	0.21630(19)	−0.08485(18)	0.0245(9)
C(22)	0.51732(19)	0.21801(16)	0.17478(17)	0.0168(8)
C(23)	0.48870(19)	0.29586(16)	0.19219(17)	0.0152(8)
C(24)	0.50624(19)	0.32329(16)	0.27250(17)	0.0165(8)
C(25)	0.48177(19)	0.39456(16)	0.28880(17)	0.0169(8)
C(26)	0.4334(2)	0.43928(16)	0.22116(17)	0.0183(8)
C(27)	0.4107(2)	0.41326(17)	0.13930(17)	0.0188(8)
C(28)	0.44023(19)	0.34215(16)	0.12596(17)	0.0174(8)
C(29)	0.3510(2)	0.46341(17)	0.06875(18)	0.0226(9)
C(30)	0.4015(3)	0.53840(19)	0.0705(2)	0.0356(11)
C(31)	0.3362(3)	0.4269(2)	−0.01668(18)	0.0339(11)
C(32)	0.2509(2)	0.47592(19)	0.07923(19)	0.0283(10)
C(33)	0.4909(2)	0.23990(17)	0.37799(19)	0.0227(9)
C(34)	0.5524(3)	0.18883(18)	0.4443(2)	0.0297(10)
C(35)	0.5014(2)	0.42730(17)	0.37551(17)	0.0193(8)
C(36)	0.5964(2)	0.40897(15)	0.44061(17)	0.0165(8)
C(37)	0.6845(2)	0.41827(15)	0.42582(17)	0.0162(8)
C(38)	0.77164(19)	0.40767(15)	0.48933(17)	0.0156(8)
C(39)	0.7658(2)	0.38339(15)	0.56592(17)	0.0161(8)
C(40)	0.6790(2)	0.36978(15)	0.58197(17)	0.0167(8)

TABLE 1 (continued)

Atom	x	y	z	U_{eq} [a]
C(41)	0.59455(19)	0.38490(16)	0.51851(17)	0.0169(8)
C(42)	0.6795(2)	0.33768(16)	0.66647(17)	0.0181(8)
C(43)	0.5772(2)	0.32825(19)	0.67358(19)	0.0253(9)
C(44)	0.7354(2)	0.39056(18)	0.73535(18)	0.0243(9)
C(45)	0.7287(2)	0.26136(17)	0.67871(19)	0.0239(9)
C(46)	0.6915(2)	0.50606(16)	0.32113(19)	0.0227(9)
C(47)	0.6907(2)	0.50366(18)	0.23138(18)	0.0258(10)
C(48)	0.87052(19)	0.42362(16)	0.47916(17)	0.0174(8)

[a] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

a partial cone. So it turns out that the crystal-structure conformation of the title compound, a partial cone with two ethoxy groups in the anti position, represents a unique case.

Molecular mechanics calculations for the analogous 1,2-dimethylether also predict that the partial cone is the most stable conformation [7].

The partial cone is strongly deformed as indicated by the interplanar angles of the four phenyl rings with the plane of the methylene C atoms: for rings A, B, C and D these angles are 73.6(1), 48.4(1), 58.0(1) and $-67.0(1)°$, respectively. Ring A is nearly perpendicular to rings B (84.0(1)°) and D (84.8(1)°), whereas rings B and D approach parallelity (18.7(1)°). The four phenyl rings are planar, the average σ_{plane} is 0.014 Å and the plane of the four linking methylene C atoms is slightly puckered (σ_{plane} = 0.157 Å). Three of the *tert*-butyl groups are staggered with respect to one of the aromatic C–C bonds (average torsion angle 176.4°) and at ring B the conformation is eclipsed (torsion angle 0.6(4)°). As in the teraethylether and mixed diethyldimethylethers [10] mentioned earlier, the ethoxy groups are oriented in such a way that the CH_2 groups point outwards and the CH_3 groups inwards, as follows from the C–O–C–C torsion angles of 177.4(2) and $-178.7(2)°$. Three of the bond angles at the bridging methylene carbon atoms are similar (118.8(2), 115.4(2) and 117.5(2)°); the angle involving rings A and B, however, is significantly smaller (108.5(2)°). The partial cone conformation is stabilized by two intramolecular hydrogen bonds. The O(1)–H group donates a bond to O(2) of the second hydroxyl group with geometries O···O 2.825(3), H···O 2.09(3) Å and O–H···O 147(3)°, the O(2)–H group donates to O(3) of a neighbouring ethoxy group with geometries O···O 2.620(3), H···O 1.71(3) Å and O–H···O 174(3)°.

TABLE 2

Bond distances (Å) and bond angles (deg.) with esd values in parentheses

Parameter	Value	Parameter	Value
Bond length			
O(1)–C(2)	1.376(3)	C(18)–C(20)	1.531(4)
O(2)–C(13)	1.378(3)	C(18)–C(21)	1.526(4)
O(3)–C(24)	1.405(3)	C(22)–C(23)	1.509(4)
O(3)–C(33)	1.433(4)	C(23)–C(24)	1.394(4)
O(4)–C(37)	1.382(3)	C(23)–C(28)	1.402(4)
O(4)–C(46)	1.423(4)	C(24)–C(25)	1.375(4)
C(1)–C(2)	1.387(4)	C(25)–C(26)	1.401(4)
C(1)–C(6)	1.393(4)	C(25)–C(35)	1.524(4)
C(1)–C(48)	1.519(4)	C(26)–C(27)	1.403(4)
C(2)–C(3)	1.393(4)	C(27)–C(28)	1.384(4)
C(3)–C(4)	1.382(4)	C(27)–C(29)	1.537(4)
C(3)–C(11)	1.519(4)	C(29)–C(30)	1.526(5)
C(4)–C(5)	1.385(4)	C(29)–C(31)	1.541(4)
C(5)–C(6)	1.398(4)	C(29)–C(32)	1.531(4)
C(5)–C(7)	1.534(4)	C(33)–C(34)	1.514(5)
C(7)–C(8)	1.522(4)	C(35)–C(36)	1.521(4)
C(7)–C(9)	1.531(4)	C(36)–C(37)	1.384(4)
C(7)–C(10)	1.542(4)	C(36)–C(41)	1.393(4)
C(11)–C(12)	1.514(4)	C(37)–C(38)	1.406(4)
C(12)–C(13)	1.385(4)	C(38)–C(39)	1.392(4)
C(12)–C(17)	1.388(4)	C(38)–C(48)	1.522(4)
C(13)–C(14)	1.399(4)	C(39)–C(40)	1.387(4)
C(14)–C(15)	1.403(4)	C(40)–C(41)	1.393(4)
C(14)–C(22)	1.520(4)	C(40)–C(42)	1.537(4)
C(15)–C(16)	1.390(4)	C(42)–C(43)	1.534(4)
C(16)–C(17)	1.394(4)	C(42)–C(44)	1.532(4)
C(16)–C(18)	1.531(4)	C(42)–C(45)	1.528(4)
C(18)–C(19)	1.530(4)	C(46)–C(47)	1.514(4)
Bond angle			
C(24)–O(3)–C(33)	114.5(2)	C(13)–C(14)–C(22)	122.2(2)
C(37)–O(4)–C(46)	117.0(2)	C(15)–C(14)–C(22)	119.6(2)
C(2)–C(1)–C(6)	119.1(3)	C(14)–C(15)–C(16)	122.1(3)
C(2)–C(1)–C(48)	120.9(3)	C(15)–C(16)–C(17)	117.7(3)
C(6)–C(1)–C(48)	120.0(2)	C(15)–C(16)–C(18)	123.7(2)
O(1)–C(2)–C(1)	118.0(2)	C(17)–C(16)–C(18)	118.5(3)
O(1)–C(2)–C(3)	121.6(2)	C(12)–C(17)–C(16)	121.8(3)
C(1)–C(2)–C(3)	120.5(3)	C(16)–C(18)–C(19)	109.6(2)
C(2)–C(3)–C(4)	118.9(3)	C(16)–C(18)–C(20)	109.7(2)
C(2)–C(3)–C(11)	122.2(2)	C(16)–C(18)–C(21)	111.8(2)
C(4)–C(3)–C(11)	118.8(2)	C(19)–C(18)–C(20)	109.3(2)
C(3)–C(4)–C(5)	122.6(3)	C(19)–C(18)–C(21)	108.1(2)
C(4)–C(5)–C(6)	117.3(2)	C(20)–C(18)–C(21)	108.3(2)
C(4)–C(5)–C(7)	119.6(2)	C(14)–C(22)–C(23)	115.4(2)

TABLE 2 (continued)

Parameter	Value	Parameter	Value
C(6)–C(5)–C(7)	123.0(2)	C(22)–C(23)–C(24)	122.3(2)
C(1)–C(6)–C(5)	121.6(3)	C(22)–C(23)–C(28)	119.5(2)
C(5)–C(7)–C(8)	112.1(2)	C(24)–C(23)–C(28)	118.1(3)
C(5)–C(7)–C(9)	109.4(2)	O(3)–C(24)–C(23)	117.7(2)
C(5)–C(7)–C(10)	109.8(3)	O(3)–C(24)–C(25)	119.7(2)
C(8)–C(7)–C(9)	108.7(3)	C(23)–C(24)–C(25)	122.6(3)
C(8)–C(7)–C(10)	107.7(2)	C(24)–C(25)–C(26)	117.6(3)
C(9)–C(7)–C(10)	109.0(3)	C(24)–C(25)–C(35)	124.4(3)
C(3)–C(11)–C(12)	108.5(2)	C(26)–C(25)–C(35)	118.0(3)
C(11)–C(12)–C(13)	119.9(2)	C(25)–C(26)–C(27)	121.9(3)
C(11)–C(12)–C(17)	120.3(3)	C(26)–C(27)–C(28)	118.3(3)
C(13)–C(12)–C(17)	119.4(3)	C(26)–C(27)–C(29)	118.9(3)
O(2)–C(13)–C(12)	116.8(2)	C(28)–C(27)–C(29)	122.8(2)
O(2)–C(13)–C(14)	122.5(3)	C(23)–C(28)–C(27)	121.4(3)
C(12)–C(13)–C(14)	120.8(3)	C(27)–C(29)–C(30)	110.1(3)
C(13)–C(14)–C(15)	118.2(3)	C(27)–C(29)–C(31)	111.6(3)
C(27)–C(29)–C(32)	109.3(2)	C(39)–C(38)–C(48)	119.0(2)
C(30)–C(29)–C(31)	108.9(3)	C(38)–C(39)–C(40)	123.2(3)
C(30)–C(29)–C(32)	109.6(3)	C(39)–C(40)–C(41)	117.2(3)
C(31)–C(29)–C(32)	107.4(3)	C(39)–C(40)–C(42)	119.6(3)
O(3)–C(33)–C(34)	107.6(3)	C(41)–C(40)–C(42)	123.2(3)
C(25)–C(35)–C(36)	118.8(2)	C(36)–C(41)–C(40)	121.8(3)
C(35)–C(36)–C(37)	122.0(2)	C(40)–C(42)–C(43)	112.2(2)
C(35)–C(36)–C(41)	118.8(3)	C(40)–C(42)–C(44)	109.2(2)
C(37)–C(36)–C(41)	119.1(3)	C(40)–C(42)–C(45)	109.5(2)
O(4)–C(37)–C(36)	119.3(3)	C(43)–C(42)–C(44)	108.3(2)
O(4)–C(37)–C(38)	119.4(3)	C(43)–C(42)–C(45)	108.4(2)
C(36)–C(37)–C(38)	121.0(3)	C(44)–C(42)–C(45)	109.3(2)
C(37)–C(38)–C(39)	117.5(3)	O(4)–C(46)–C(47)	106.2(2)
C(37)–C(38)–C(48)	123.5(2)	C(1)–C(48)–C(38)	117.5(2)

Infrared

The FT-IR spectra of the *anti*-1,2-diethoxy-*p*-*tert*-butylcalix[4]arene (ADET) in fluorolube mull are presented for two different temperatures (300 and 100 K) in Fig. 3 for the OH stretching region. Figures 4 and 5 show ADET and its syn analogue (SDET) in dilute CCl_4 and CS_2 solution, respectively.

Solid

Spectra were recorded from ambient temperature down to 100 K in five steps, firstly to check for solid–solid phase changes and secondly to get

TABLE 3

Torsion angles (deg.) about the $C(sp^3)$–$C(sp^2)$ bonds[a]

Angle	Value	
C(4)–C(3)–C(11)–C(12)	−72.9(3)	A–B
C(3)–C(11)–C(12)–C(17)	94.6(3)	
C(15)–C(14)–C(22)–C(23)	−96.7(3)	B–C
C(14)–C(22)–C(23)–C(28)	90.6(3)	
C(26)–C(25)–C(35)–C(36)	−142.4(3)	C–D
C(25)–C(35)–C(36)–C(41)	−131.3(3)	
C(39)–C(38)–C(48)–C(1)	132.1(3)	D–A
C(38)–C(48)–C(1)–C(6)	129.2(3)	

[a] Torsion angles all involve a C atom at the meta position.

information about the temperature dependence of the OH stretching frequencies for the intramolecular O–H···O hydrogen bonds. The second point seems to be of particular interest since intramolecular H···O distances and corresponding OH frequencies should hardly be influenced by temperature [21]. The spectra in Fig. 3 exhibit two intense bands at 3388.0 and 3175.0 cm^{-1} at 300 K and 3394.5 and 3129.0 cm^{-1} at 100 K. The corresponding halfbandwidths are 41 and 80 cm^{-1} for ambient temperature and 13 and 32 cm^{-1} for 100 K. Additionally, we observed a shoulder on the high frequency side of the 3175 cm^{-1} band at 3217 cm^{-1} (from second derivative). In the low temperature spectrum (Fig. 3b) this band is not overlapped any more by the OH mode at 3129 cm^{-1} and it is therefore assigned to an overtone or combination band.

Frequency shifts relative to the corresponding 'free' OH ($\Delta\bar{\nu}$) usually serve as a synonym for hydrogen-bond strength, and bond distances less than the sum of the van der Waals contact radii are taken as geometrical criteria for the formation of hydrogen bonds in solids. The existence of a direct relationship between these quantities has been shown by Novak [22] and Mikenda [23]. For the 'free' phenolic OH group of *p-tert*-butylphenol in CCl_4, which can serve as a realistic reference, Lutz and van der Maas [24] observed a stretching frequency of 3613 cm^{-1} with a halfbandwidth of 16 cm^{-1}. It therefore seems to be straightforward to assign the high frequency band at 3388 cm^{-1} ($\Delta\bar{\nu}$ = 225 cm^{-1}) to the O(1)–H···O(2)–H interaction (O···O 2.825 Å) and the low frequency mode at 3175 cm^{-1} ($\Delta\bar{\nu}$ = 438 cm^{-1}) to the shorter O(2)–H···O(3)–Et hydrogen bond (O···O 2.620 Å). This assignment is further supported by the unfavourable O–H···O angle (147°) of the O(1)–H···O(2) hydrogen bond which strongly deviates from the preferred linear hydrogen-bond geometry [25, 26]. Especially for this bent hydrogen bond, a drastic decrease of the halfbandwidth can be

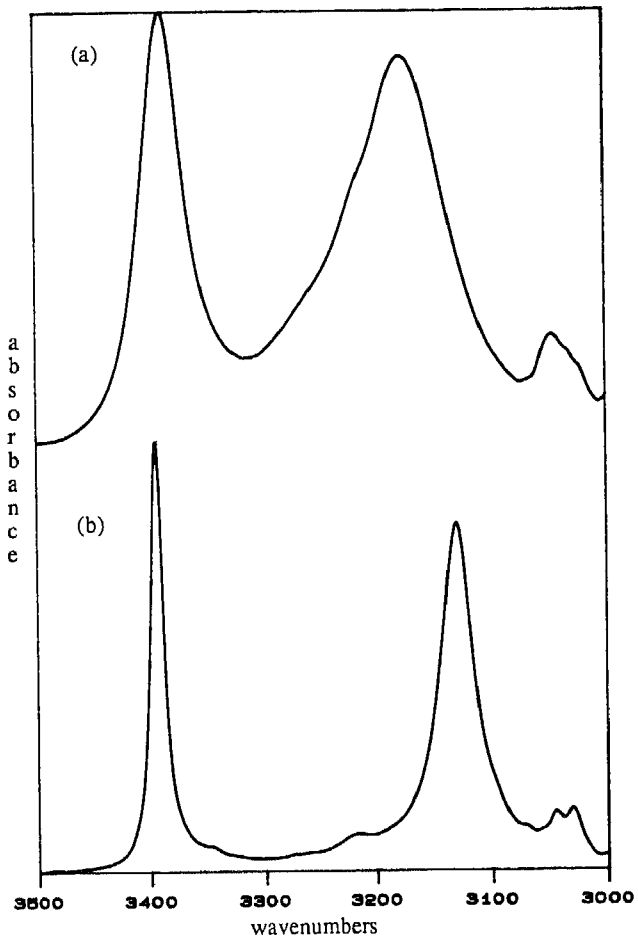

Fig. 3. FT-IR spectra of ADET in fluorolube mull in the 3500–3000 cm^{-1} range at 300 K (a) and 100 K (b).

observed upon cooling (about 70%), which is far more than the 40% found for an intermolecular O–H···O hydrogen bond of similar geometry (O···O 2.839 Å and O–H···O 143°) and frequency 3367 cm^{-1} ($\Delta\bar{\nu} = 246\,cm^{-1}$) in 2-ethynyladamantan-2-ol [27]. It seems to indicate a better localization of the O–H···O system in the studied compound. Additionally we calculated the temperature coefficients of frequency ($\frac{d\bar{\nu}}{dT}$) by plotting the values of the band maxima against temperature and no discontinuity, indicative for a phase change, could be observed. The maximum of the low frequency band shifts from 3175 (300 K) to 3129 cm^{-1} at 100 K ($\frac{d\bar{\nu}}{dT} = +0.237\,cm^{-1}\,K^{-1}$; $R^2 = 0.987$) whereas that of the high frequency mode shifts slightly in a smooth but non-linear way from 3388 (300 K) to 3394.5 cm^{-1} (100 K). This

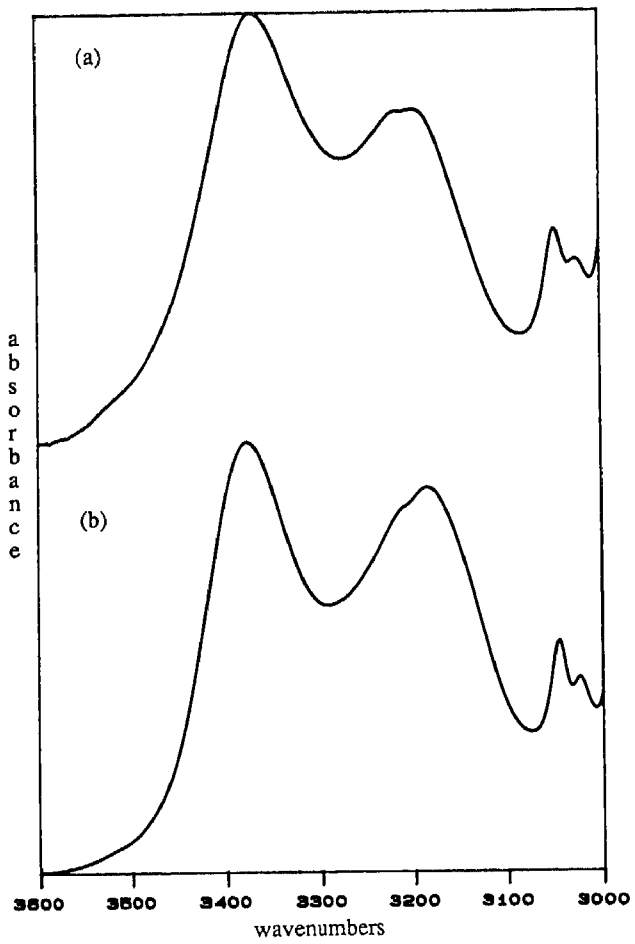

Fig. 4. FT-IR spectra of ADET in the 3600–3000 cm^{-1} range in CCl_4 (a) and CS_2 (b).

large positive value is remarkable for an intramolecular hydrogen bond as its order of magnitude is comparable to the values found for intermolecular O–H··O hydrogen-bonded systems of comparable strength [21, 27]. The main effect causing the low frequency shift of the OH stretching mode in intermolecular hydrogen bonds upon cooling is thought to be the strengthening of the hydrogen bond by a reduction of the O···O distance. Recently Slootmaekers and Desseyn [21] reported that temperature lowering has a much more pronounced effect on the strength of a short hydrogen bond than on a long one. Taking these results into account, together with the opposite sign of the temperature coefficient of frequency for the two intramolecular O–H···O hydrogen bonds in ADET, we conclude that the partial cone, characteristic for the solid state, seems to change its conformation

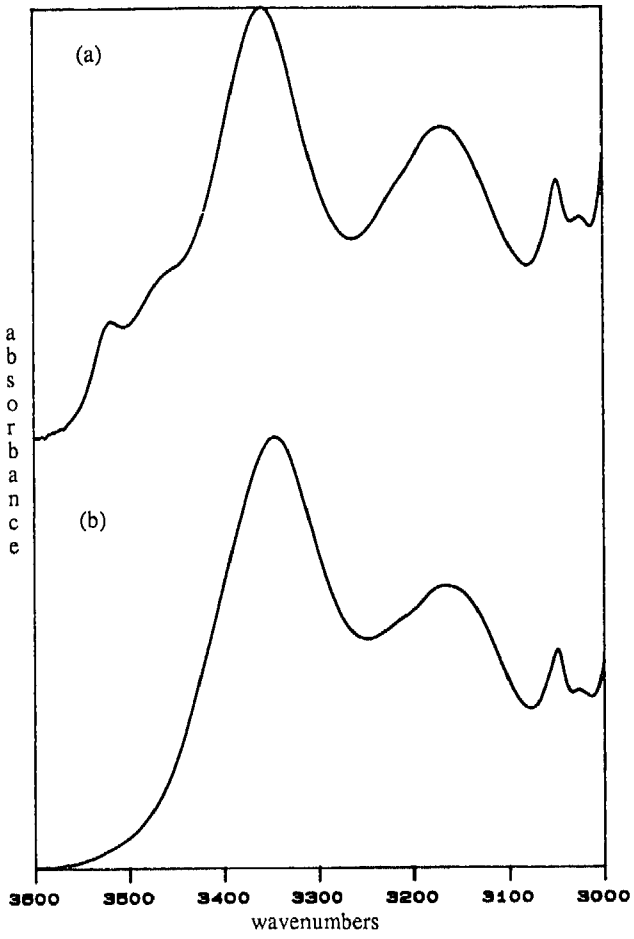

Fig. 5. FT-IR spectra of SDET in the 3600–3000 cm^{-1} range in CCl_4 (a) and CS_2 (b).

slightly upon cooling, with the stronger O(2)–H···O(3) hydrogen bond becoming shorter at the expense of the weaker O(1)–H···O(2) interaction. Another factor worth mentioning might be that the cooperativity in the O(1)–H···O(2)–H···O(3)–Et system becomes more pronounced on cooling because of the reduced thermal vibrations (especially OH bending modes) and thus favours the O(2)···O(3)–Et hydrogen bond.

Solution

The solution IR spectra of ADET (Fig. 4) have been measured in CCl_4 as well as in CS_2 at ambient temperature. Two rather broad, overlapping bands can be observed and therefore we used second derivative spectroscopy for the location of the band maxima. In CCl_4 the two OH stretching

modes are found at 3378 and 3187 cm^{-1}, and in CS_2 at 3386 and 3182 cm^{-1}. Their halfbandwidths range from about 130 to 150 cm^{-1} in CCl_4, but are somewhat smaller in CS_2 and much larger than the halfbandwidths of the solid compound. However, the solid state spectra in Fig. 3a, characterizing the partial cone conformation, and the solution spectra (Fig. 4) agree very well in both physical states. This observation leads to the assumption that the partial cone structure, together with a hydrogen-bond geometry comparable to that found for the solid state, is preserved in apolar solution. However, it has been deduced from ^1H NMR that ADET is characterized by a 1,2-alternate conformation with one of the ethoxy groups and its neighbouring hydroxyl groups on one side of the ring and the other ethoxy and hydroxyl groups on the other side [10]. This conformer would also exhibit two hydrogen bonds, but the following points support the partial cone structure.

(1) The identity of the band maxima in solid phase and solution.

(2) The O···O distance of the ether groups on the same and opposite sides of the ring in tetrasubstituted calix[4]arenes adopting the 1,2-alternate conformation in solid state proves to be equal [11] or very similar [10]. Even if the hypothetical 1,2-alternate of ADET would exhibit asymmetry of the two O–H···O–Et hydrogen bonds, the difference in frequency observed in solution (about 200 cm^{-1}) is exceptionally large.

(3) So far $\tilde{\nu}_{OH}$ values lower than 3200 cm^{-1} have only been found for calix[4]arenes when at least two neighbouring OH groups form an O–H···O–H hydrogen-bond system in which the O–H···O hydrogen bonds are strengthened by cooperativity [28].

(4) For isolated O–H···O–Me hydrogen bonds in 1,3-dimethoxy-*p-tert*-butylcalix[4]arene, Araki et al. [28] report an OH stretching frequency of 3450 cm^{-1}.

An alternative interpretation of the ^1H NMR spectrum could be that the observed signals are the time-averaged signals of two equivalent partial cones that are interconverting by simultaneous rotation of both phenol rings.

Considering the above-mentioned results for the *anti*-1,2-diethylether, one would expect a cone conformation for the corresponding *syn*-1,2-diethylether (SDET) with two different O–H···O hydrogen bonds. Indeed Fig. 5 shows two different OH stretching bands for SDET in CCl_4 (3360 and 3168 cm^{-1}) as well as in CS_2 (3345 and 3165 cm^{-1}). The somewhat lower wavenumbers compared to ADET indicate that the cone structure seems to be more symmetric and favours stronger hydrogen bonds than the partial cone structure of the corresponding anti compound. Furthermore, the spectrum of SDET in CCl_4 (Fig. 5a) exhibits two additional bands at 3525 and 3468 cm^{-1} of low intensity, which overlap with the broad absorption on the high frequency side. Surprisingly, both bands are not present in the CS_2

solution spectrum (Fig. 5b). This brings us to the assumption that SDET adopts, next to the dominating cone, another conformation in CCl_4, resulting from the rotation of one or both OH groups through the annulus of the calix[4]arene. Two distinct conformers could result, a partial cone or a 1,2-alternate, both characterized by a different hydrogen-bonding scheme. The partial cone would exhibit an O–H···O–Et hydrogen bond and a 'free' OH group or an OH group hydrogen-bonded to the π-system of the neighbouring phenyl rings (O–H···π), while the 1,2-alternate would be characterized by one O–H···O–H hydrogen bond and one 'free' or O–H···π-bonded OH group. Although the observed frequency of 3525 cm^{-1} agrees well with the usual values found for O–H···π hydrogen bonding [29], it is not possible to assign the 3468 cm^{-1} band unambiguously to an O–H···O–Et or O–H···O–H hydrogen bond, thus leaving open the question about the nature of the second conformation of SDET in CCl_4 for further discussion.

The striking difference of the CCl_4 and CS_2 spectra can be understood taking into account that *p-tert*-butylcalix[4]arenes contain enforced cavities large enough to admit solvent molecules [30]. The limited diameter of these cylindrical wells denies occupancy to the larger CCl_4 molecule but allows CS_2 to penetrate deeply into the host cavity, as was shown by Cram et al. [31] for similar cavitands and CS_2. Cram et al. [32] also stated that most host–guest complexes are more rigid than the host and guests taken separately, which, applied to our SDET–CS_2 system, would mean that the cone conformation in solution is not solely stabilized by intramolecular hydrogen bonds but also via the formation of a host–guest complex with the CS_2 inside the apolar cavity.

CONCLUSIONS

In this paper we have tried to clarify how the conformation of *p-tert*-butylcalix[4]arene changes upon partial 1,2-di-O-ethyl substitution. Infrared solution spectra indicate that the 1,2-syn isomer favours the cone conformation, which is stabilized by the formation of two intramolecular hydrogen bonds. Intramolecular hydrogen bonding is also the driving force in establishing the cone conformation of the 1,3-syn isomer [10]. In the 1,2-anti isomer, of which the crystal structure is reported, a cone is impossible because of the anti arrangement of the two ethoxy-phenyl groups. Instead, the compound is seen to exist in the partial cone conformation, which in contrast to the also possible 1,2-alternate form, allows the formation of a cooperative system of two intramolecular hydrogen bonds.

Infrared solution and solid state spectra of the 1,2-anti isomer are in agreement with the observed crystal-structure conformation. The discrepancy between the interpretation of infrared solution spectra and ^1H NMR spectra, which indicated a 1,2-alternate [10], may be explained by the

interconversion of equivalent partial cones, a process which is frozen out on the IR time scale, but not on the ^1H NMR time scale.

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