

Journal of Molecular Structure 354 (1995) 227-231



2,3-Dimethoxynaphthalene: solid-state structure as studied via X-ray crystallography and solid-phase ¹³C nuclear magnetic resonance spectroscopy

G.W. Buchanan*, M. Gerzain, C. Bensimon

Ottawa-Carleton Chemistry Institute, Department of Chemistry, Carleton University, Ottawa, Ont., K1S 5B6, Canada

Received 8 January 1995; accepted 22 February 1995

Abstract

The X-ray crystal structure of the title material has been obtained. A symmetrical structure with the OCH₃ groups essentially planar to the aromatic ring has been found. Chemical shift differences observed in the solid-state ¹³C cross polarization/magic angle spinning spectrum are attributed to intermolecular crystal packing effects, resulting in an asymmetric unit of one molecule.

1. Introduction

A good deal of effort has been expended on the unambiguous assignment of the solution-phase ${}^{13}C$ NMR spectra of polysubstituted naphthalenes [1,2]. In addition, some preliminary solid-state 13 C NMR data have been reported for a series of 1,2-dialkoxybenzenes [3]. Proper analysis of solidphase ¹³C spectral multiplicity, however, is dependent upon the availability of X-ray crystallographic data, since non-averaged conformations, nonequivalent molecules in the unit cell and intermolecular crystal packing effects can all lead to increased solid-phase multiplicity compared to that observed in solution [4]. In order to more properly document such effects in these classes of materials, we report herein the X-ray crystal structure of 2,3-dimethoxynaphthalene (1), as well as its solid-phase ¹³C chemical shifts. Shift differences in

the solid are discussed in light of the results from X-ray diffraction and the structure is discussed in comparison with data for related *ortho*-dimethoxy aromatics.

2. Experimental

2.1. Materials

A sample of 2,3-dimethoxynaphthalene was prepared according to the following method. Dimethylsulfate (Aldrich) (25.2 g, 0.2 mol) was added to 2,3-dihydroxynaphthalene (Aldrich) (16 g, 0.1 mol) in 65 ml of a 15% aqueous NaOH solution with stirring. Precipitation of the solid product was immediately evident. The reaction mixture was stirred and refluxed for 2 h. After cooling, the solid product was removed by suction filtration. The mother liquor was extracted with CH_2Cl_2 , and the organic extract was subsequently

^{*} Corresponding author.

^{0022-2860/95/\$09.50 © 1995} Elsevier Science B.V. All rights reserved SSDI 0022-2860(95)08871-7

washed with 2% KOH followed by a saturated NaCl solution, before being dried over anhydrous sodium sulfate. The solvent was removed via evaporation at reduced pressure to give a crude solid. The solid products were then combined and recrystallized from methanol to give 14.2 g (75.5%) of long clear needles, m.p. $112-113^{\circ}$ C.

2.2. Solid-phase ¹³C NMR

The ¹³C cross polarization/magic angle spinning (CP/MAS) spectrum was obtained at 45.3 MHz using a Bruker CXP-180 spectrometer and a Doty Scientific MAS probe. The sample was contained in a 7 mm zirconia rotor with a Kel-F end cap. ¹H 90° pulse lengths were typically 4.5 μ s and the spinning rate was 4–5 kHz. Chemical shifts were measured relative to external hexamethylbenzene (HMB) and then converted to the TMS scale (HMB methyl resonance at 16.9 ppm).

Table 1 Crystallographic data 2.3. Crystallographic structure and structure solution

A summary of the crystal data is presented in Table 1. The intensity data were obtained at -110° C using a Rigaku diffractometer and the $\theta/2\theta$ scan mode. All atoms were refined anisotropically, except for hydrogens which were refined isotropically. Weights based on counting statistics were used and all calculations were performed with the NRCVAX crystallographic software package [5].

3. Results and discussion

The ORTEP plot and numbering scheme for 1 is presented in Fig. 1, while the crystal packing diagram is depicted in Fig. 2. The solid-phase $^{13}C CP/$ MAS NMR spectrum is shown in Fig. 3. Table 2 contains atomic bond lengths and angles, while torsion angles are presented in Table 3. Crystal-

Formula	$C_{12}H_{12}O_2$
fw	188.22
Crystal system	Orthorhombic
Space group	P 21 21 21
a (Å)	12.2873(7)
b (Å)	13.1725(8)
c (Å)	6.0278(5)
$V(\dot{A}^3)$	975.63(7)
Z (molecules per cell)	4
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.281
Crystal dimensions (mm)	0.20 imes 0.20 imes 0.20
Radiation (λ , Å)	ΜοΚα, 0.70930
Octants measured	h(0 to +14), k(0 to 15), l(0 to 7)
Max 2 θ (deg)	49.9
Temperature (°C)	-110
No. of unique reflections	1026
No. of reflections measured	1026
No. of reflections with $I_{\text{net}} > 2.5\sigma I_{\text{net}}$	886
$I\sigma/I$ ratio	0.121
<i>R</i> _f	0.027
R _w	0.030
GoF	1.57
Maximum and minimum residual	
e, respectively in final difference Fourier map ($Å^{-3}$)	0.120 and -0.150



Fig. 1. ORTEP plot for 1.

lographic data are collected in Table 1, with atomic parameters in Table 4. Structure factor tables and anisotropic temperature factors are deposited with the B.L.L.D. as Supplementary Publication No. SUP26535 (8 pages). Table 5 contains ¹³C chemical shifts.

3.1. X-ray crystal structure

The ORTEP plot (Fig. 1) and data in Tables 1–3 show that 1 appears to adopt a symmetrical structure with the OCH₃ groups lying almost in the plane of the aromatic rings. The torsional networks which illustrate the OCH₃ stereochemistry are C11–O1–C2–C1 and C12–O2–C3–C4. These units possess torsion angles of $-2.8(1)^{\circ}$ and $-3.6(1)^{\circ}$, respectively. In addition, the C11–O1– C2–C3 and C12–O2–C3–C2 networks are transoid, with torsion angles of 177.6(2)° and 176.7(2)°, respectively. A survey of the literature



Fig. 2. Crystal packing diagram for 1.



Fig. 3. 45.3 MHz ¹³C CP/MAS NMR spectrum of 1.

indicates that no previous X-ray crystallographic results have been reported for materials containing the 2,3-dimethoxynaphthalene moiety, but a substantial amount of work has been carried out on structures containing the related *ortho*dimethoxybenzene structure [6–9]. Of the 32 structures reported, 30 contain nearly planar methoxy groups.

Based on intramolecular effects alone, one would expect an effective plane of symmetry in 1, which would render the asymmetric unit as one half of the molecule. The crystal packing diagram shown in Fig. 2, however, illustrates that this is not the case. The asymmetric unit in the crystal is, in fact, one molecule, in which each carbon has a

Table 2a Atomic bond distance (Å)

	· · · · · · · · · · · · · · · · · · ·	
01-C2	1.368(2)	
O1-C11	1.432(3)	
O2–C3	1.367(2)	
O2-C12	1.436(3)	
C1-C2	1.364(3)	
C2-C3	1.434(3)	
C1-C9	1.424(3)	
C3-C4	1.366(3)	
C4-C10	1.430(3)	
C5-C6	1.367(3)	
C5-C10	1.414(3)	
C6-C7	1.402(3)	
C7-C8	1.367(3)	•
C8-C9	1.413(3)	
C9-C10	1.421(3)	
		· · · · · · · · · · · · · · · · · · ·

Table 4

Table 2b Atomic bond angles (deg)

C2-O1-C11	116.6(2)	
C3-O2-C12	116.8(2)	
O1C2C1	125.6(2)	
O2-C3-C4	125.9(2)	
O1-C2-C3	114.1(2)	
O2-C3-C2	114.1(2)	
C1-C2-C3	120.3(2)	
C2-C3-C4	120.0(2)	
C6-C5-C10	120.6(2)	
C3-C4-C10	121.0(2)	
C1-C9-C8	121.9(2)	
C4-C10-C5	122.3(2)	
C1-C10-C9	119.5(2)	
C8-C9-C10	118.6(2)	
C4-C10-C9	118.6(2)	
C5-C10-C9	119.1(2)	
C7-C8-C9	120.9(2)	
C2-C1-C9	120.6(2)	
C6-C7-C8	120.4(2)	
C5-C6-C7	120.3(2)	

unique environment. The intermolecular interactions are deemed to be of the C-H $\cdots \pi$ type between adjacent molecules in the crystal. The internuclear C-H \cdots C distances are of the order of 2.67 Å, i.e. slightly shorter than the sum of the van der Waals radii for H and C. Similar close intermolecular contact has been found in the crystal structure of β -triketomethane [10].

Table 3			
Selected	torsion	angles	(deg)

C11-O1-C2-C1	-2.8(1)	
C12-O2-C3-C4	-3.6(1)	
O1-C2-C1-C9	-180.0(1)	
C3-C2-C1-C9	-0.4(1)	
01-C2-C3-O2	-0.4(1)	
C1-C2-C4-O2	180.0(2)	
C2-C1-C9-C8	-177.9(2)	
C9-C10-C4-C3	0.1(1)	
C10-C4-C3-O2	-179.8(2)	
C11-O1-C2-C3	177.6(2)	
C12-O2-C3-C2	176.7(2)	
O1-C2-C3-C4	179.9(2)	
C2-C1-C9-C10	0.3(1)	
C1-C9-C10-C4	-0.2(1)	
C6-C5-C10-C4	-178.7(2)	
C10-C4-C3-C2	-0.1(1)	

Atomic parameters x, y, z and Biso. ESDs refer to the last digit printed

	а	у	Ζ	Biso ^a
01	0.43187(11)	0.89795(10)	0.03811(23)	3.10(6)
O2	0.38386(10)	1.00420(11)	-0.30179(23)	3.21(6)
C1	0.58959(15)	1.00153(14)	0.1269(3)	2.39(8)
C2	0.50133(15)	0.97720(13)	0.0003(3)	2.35(7)
C3	0.47412(14)	1.03717(13)	-0.1904(3)	2.39(8)
C4	0.53693(14)	1.11877(14)	-0.2465(3)	2.48(8)
C5	0.69586(15)	1.23081(14)	-0.1695(3)	2.76(8)
C6	0.78558(16)	1.25320(15)	-0.0447(4)	3.12(9)
C7	0.81367(15)	1.19217(15)	0.1372(4)	3.17(9)
C8	0.75013(16)	1.11119(14)	0.1952(3)	2.74(8)
C9	0.65630(14)	1.08615(13)	0.0712(3)	2.26(7)
C10	0.63011(15)	1.14598(13)	-0.1174(3)	2.28(7)
C11	0.45752(17)	0.83306(15)	0.2214(4)	3.37(9)
C12	0.34884(16)	1.06428(16)	-0.4874(4)	3.29(9)
Hl	0.6070(14)	0.9582(12)	0.256(3)	3.4(4)
H4	0.5205(14)	1.1599(13)	-0.383(3)	3.3(4)
H5	0.6746(12)	1.2775(12)	-0.307(3)	2.5(4)
H6	0.8343(13)	1.3151(12)	-0.084(3)	2.6(4)
H7	0.8773(14)	1.2070(12)	0.226(3)	3.6(5)
H8	0.7661(13)	1.0693(11)	0.326(3)	2.8(4)
HIIA	0.3988(15)	0.7810(13)	0.221(3)	4.3(5)
HIIB	0.5333(15)	0.8023(13)	0.201(4)	4.9(5)
HIIC	0.4534(14)	0.8725(12)	0.363(3)	3.5(4)
H12A	0.2833(15)	1.0312(13)	-0.544(3)	4.3(5)
H12B	0.4070(16)	1.0717(13)	-0.607(3)	4.8(5)
H12C	0.3266(15)	1.1398(14)	-0.446(4)	4.6(5)

^a Biso is the mean of the principal axes of the thermal ellipsoid.

Table 5 13 C NMR chemical shifts (∂_c from TMS ± 0.1)

	Solid phase	Solution (0.1 M in CDCl ₃)
CI	105.8ª	106.3
C2	150.4	149.4
C3	150.4	149.4
C4	106.7 ^a	106.3
C5	126.8 ^b	127.0
C6	123.8	124.6
C7	123.8	124.6
C8	128.0 ^b	127.0
C9	129.7 ^c	130.2
C10	130.0 ^c	130.2
C11	54.8 ^d	55.8
C12	55.0 ^d	55.8

^{a-d} Denote possible assignment interchange.

3.2. ¹³C NMR spectra

The ¹³C NMR chemical shift data are presented in Table 5. For 1, the solution ¹³C spectrum has been unambiguously assigned with the aid of selectively deuterated molecules [2], and our solution data agree with the published values within 0.2 ppm. In the case of the solid-phase spectrum, all the chemical shifts are within 1.8 ppm of those for corresponding carbons in the solution spectrum. Solid-phase spectral differences between sites which are equivalent in the solution range from 0.2 to 1.2 ppm. In two instances, i.e. C2, C3 and C6, C7, no shift difference can be resolved in the solid-state spectrum. In summary, the solid-phase ¹³C spectral multiplicity is consistent with the observation that the asymmetric unit is one molecule. For the two pairs of sites mentioned above, the chemical shift difference is simply too small to be resolved.

Finally, it should be noted that results of differential scanning calorimetry show that there are no solid-phase changes in 1 between the temperature at which the X-ray structure was obtained

References

- W. Kitching, M. Bullpitt, D. Doddrell and W. Adcock, Org. Magn. Resonance, 6 (1974) 289.
- [2] J. Seita, J. Sandstrom and T. Drakenberg, Org. Magn. Resonance, 11 (1978) 239.
- [3] G.W. Buchanan, A.B. Driega and C.I. Ratcliffe, Magn. Resonance Chem., 31 (1993) 1094.
- [4] P.S. Belton, S.F. Tanner, K.M. Wright, M.P. Payne, M.R. Truter and J.N. Wingfield, J. Chem. Soc., Perkin Trans. 2, (1985) 1307.
- [5] E.J. Gabe, F.L. Lee and Y. LePage, J. Appl. Crystallogr., 22 (1989) 3.
- [6] G.M. Anderson, P.A. Kollman, L.M. Domelsmith and K.N. Houk, J. Am. Chem. Soc., 101 (1979) 2344.
- [7] J. Caillet, Acta Crystallogr., Sect. B, 38 (1982) 1786.
- [8] S.C. Nyburg and C.H. Faerman, J. Mol. Struct., 140 (1986) 347.
- [9] W. Hummel, K. Huml and H.-B. Burge, Helv. Chim. Acta, 71 (1988) 1291.
- [10] M.C. Etter and G.M. Vogta, J. Magn. Resonance, 93 (1991) 609.