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Synthesis, Raman spectrum, ab initio calculations, and structure of 3,7-dioxabicyclo[3.3.0]oct-1,5-ene

Cornelia Mlynek^a, Henning Hopf^a, Juan Yang^b, Jaan Laane^{b,*}

^aInstitut für Organische Chemie, Technische Universität, D-38106 Braunschweig, Germany ^bDepartment of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA

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Abstract

The bicyclic bisether molecule 3,7-dioxabicyclo[3.3.0]oct-1,5-ene (DOBO) molecule has been synthesized in small quantities and has been shown to be analytically pure by NMR and mass spectra. The vapor-phase Raman spectrum has been analyzed and compared to the predicted spectra from DFT calculations. This spectrum further confirms the structure of the molecule and shows the skeleton of both rings to be planar with D_{2h} symmetry. Ab initio calculations were carried out to predict the bond distances and angles of the molecule, and these also showed the molecule to be planar.

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1. Introduction

We have previously reported [1] the vibrational spectra and ab initio calculations for bicycle[3.3.0]oct-1,5-ene (BCO). This molecule is structurally interesting in that the two five-member rings can pucker in either the same or opposite directions producing either *cis* ($C_{2\nu}$) or *trans* (C_{2h}) structures. Because the barriers to inversion are small, the vibrational spectra can be described quite well on the basis of a planar (D_{2h}) structure. Nonetheless, the spectra and ab initio calculations both show the *cis* $C_{2\nu}$ conformation to be the lowest energy form. The C_{2h} *trans* form is slightly higher in energy but still about 1 kcal/mole more stable than the planar structure.



In the present paper, we present the method of preparation for 3,7-dioxabicyclo[3.3.0]oct-1,5-ene (DOBO) as well as its Raman spectrum. This molecule

has been synthesized before (see below), but we were interested in studying its vibrational spectrum, structure, and the nature of its ring-puckering motions. The ringpuckering spectra of BCO are expected to be very complicated, and because the vibrations do not have much of dipole moment changes, they are expected to be weak [1,2]. DOBO, on the other hand, will have a large dipole moment change for the in-phase puckering, and its spectra should be simpler as the planar form should be the most stable.

For this initial report only 15 mg of DOBO were prepared and this only allowed its vapor-phase Raman spectrum to be recorded. Because of the small amount of sample, no other spectra were recorded. Together with ab initio calculations, the Raman spectrum was used to determine the symmetry and structure of the molecule.

2. Experimental

Raman spectra of the DOBO vapor at a temperature of 250 °C were recorded using an Instruments SA JY-U1000 spectrometer and a Coherent Radiation Innova 20 argon ion laser with excitation at 514.5 nm and 4 W laser power.

^{*} Corresponding author. Tel.: +1 979 845 3352; fax: +1 979 845 3154. *E-mail address:* laane@mail.chem.tamu.edu (J. Laane).

A liquid nitrogen cooled charge-coupled device (CCD) was used as the detector. The spectral resolution was 0.7 cm^{-1} with the CCD. The sample was contained in a high-temperature Raman cell previously described [3]. The sample pressure was about 700 Torr.

3. Synthesis

The title compounds was essentially prepared by the route described by Ripoll [4], and this is shown in Scheme 1. Thus the Diels–Alder adduct **3** was prepared by cycloaddition of tetraethyl ethylentetracarboxylate **2** (Lancaster Chemicals) to anthracene **1**. LiAlH₄ reduction of **3** then provided the tetraalcohol **4** which on heating in DMSO [5] for extended periods of time was dehydrated to furnish the bisether **5**.

Although the thermal fragmentation of 5 by high temperature vacuum pyrolysis yielded the starting material 1 in quantitative yield, the isolated amounts of the title compound 6 varied and were much smaller. We believe that this was due to the design of our pyrolysis system the tube of which was much longer than the one employed in the original literature [4]. Contact time was hence longer and material lost by subsequent thermal reactions. The bisether was purified in a two-step approach: filtration over silica gel with pentane first allowed the removal of anthracene, and after 6 had been isolated from the column by ether extraction it was purified by vacuum sublimation (50 °C, 15 Torr). MS and NMR analysis showed the material to be analytically pure (¹H NMR (200.1 MHz, CDCl₃): $\delta =$ 4.54 (s). $-^{13}$ C NMR (50.3 MHz, CDCl₃): $\delta = 70.15$ (t), 141.67 (s).





4. Computations

Ab initio calculations were carried out using the GAUSSIAN 03 package at both the Moller–Plesser secondorder perturbation (MP2) and the density functional (B3LYP) levels of theory with various basis sets. Energies and structural parameters were calculated using the MP2 theory with the CC-pVTZ (triple zeta) basis set, while the vibrational frequencies with both the infrared and Raman intensities were obtained with the density functional (B3LYP) method and the 6-311++G** basis set. The frequency scaling factors are 0.964 for the 2800–3000 cm⁻¹ region and 0.985 for the region below 1700 cm⁻¹.

5. Results and discussion

Fig. 1 shows the vapor-phase Raman spectrum of 3,7dioxabicyclo[3.3.0]octane-1(5) (DOBO) recorded at 250°. The sharp, more intense bands all correspond to the totally symmetric A_g vibrations in D_{2h} symmetry. The broader band types correspond to B_{1g} , B_{2g} , and B_{3g} modes. All other vibrations are Raman inactive. Due to lack of sample, no infrared spectra were recorded and thus the frequencies for the infrared active ungerade modes were not determined experimentally. Density functional theory (DFT) computations were used to calculate both the structure and Raman spectrum of this molecule, and Fig. 1 also compares the computated spectrum to the experimental one. The computed spectrum assumes Lorentzian band shapes and therefore makes no attempt to predict the vapor-phase band types. The frequency agreement between the recorded spectrum and calculated spectrum is excellent; the intensity agreement is



Fig. 1. Vapor-phase Raman spectrum of DOBO at $250 \,^{\circ}$ C (top) and calculated Raman spectrum using the B3LYP/6-311++G** basis set (bottom).

Table 1 Vibrational assignments (cm⁻¹) for the Raman active (gerade) modes of 3,7-dioxabicyclo[3.3.0]oct-1,5-ene

Symmetry D _{2h}	$v(D_{2h})$	Description	Raman				Ab initio ^a	
			Vapor ^b		BCO vapor	r ^{b,c}	$D_{2h}^{b,d}$	
$\overline{A_g}$	1	CH_2 sym. stretch (ip, ip')	2870	(100)	2857	(100)	2887	(100)
R:P	2	C=C stretch	1690	(4)	1677	(27)	1716	(5)
	3	CH_2 deformation (ip, ip')	1486	(10)	1473	(17)	1501	(8)
	4	CH_2 wag (ip, op')	1350	w	1287	(5)	1363	(0.7)
	5	Ring stretch	897	(7)	889	(22)	887	(2)
	6	Ring breathing (ip')	857	(2)	852	(14)	863	(0.2)
	7	Ring bend (ip, ip')	537	(4)	522	(7)	535	(1)
B_{1g}	8	CH_2 sym. stretch (op, op')	(2870) ^e	_	(2857) ^e	_	2877	(18)
R:D	9	CH_2 deformation (op, op')	1469 sh	(4)	-	-	1488	(4)
	10	CH_2 wag (op, ip')	1385	vw	_	_	1392	(1)
	11	Ring stretch	1237	(1)	-	-	1235	(0.8)
	12	Ring stretch	1018	W	968	vw	1013	(0.2)
	13	Skeletal bend (op, op')	683	(1)	676	vw	676	(0.3)
B_{2g}	14	CH_2 antisym. stretch (ip, op')	2902	(5)	2954	(42)	2900	(10)
R:D	15	CH_2 twist (ip, ip')	1148	(2)	_	_	1130	(2)
	16	CH_2 rock (ip, op')	941	w	_	_	932	(0.4)
	17	Ring puckering (op')	-	-	-	_	115	(0.1)
B_{3g}	18	CH_2 antisym. stretch (op, ip')	2886	(5)	2874	vw	2899	(57)
R:D	19	CH_2 twist (op, op')	1201	(1)	_	_	1203	(1)
	20	CH_2 rock (op, ip')	1071	vw	_	_	1074	(0.3)
	21	Ring twisting (ip')	450	(2)	-	-	449	(0.0)

ip, in-phase; op, out-of-phase; w, weak; v, very; sh, should; R, Raman; P, polarized; D, depolarized.

^a Calculated using the B3LYP/6-311 + +G(d,p) basis set. ^b Relative intensity in parenthesis.

^c From Ref. [1]. ^d Frequency scaled with a scaling factor of 0.985 for frequencies less than 1800 cm⁻¹ and 0.964 for frequencies greater than 2800 cm⁻¹.

Table 2 Calculated vibrational frequencies (cm⁻¹) for the ungerade modes of 3,7-dioxabicyclo[3.3.0]oct-1,5-ene (DOBO) compared to bicyclo[3.3.0]oct-1,5-ene (BCO)

Symmetry D_{2h}	v (D _{2h})	Description CH ₂ antisym. stretch (op, op')	Ab initio ^a				
			DOBO $(D_{2h})^{b}$		BCO $(C_{2\nu})^c$		
A_{u}			2898	(0)	2896	(47)	
	23	CH_2 twist (op, ip')	1189	(0)	1219	(0.86)	
	24	CH_2 rock (op, op')	999	(0)	865	(0.37)	
	25	Ring twisting (op')	209	(0)	191	(0)	
B_{1u}	26	CH_2 antisym. stretch (ip, ip')	2901	(54)	2891	(19)	
	27	CH_2 twist (ip, op')	1172	(1.6)	1217	(2.5)	
	28	CH_2 rock (ip, ip')	1025	(2.8)	1067	(1.6)	
	29	Ring flapping (ip')	166	(0.78)	207	(4.2)	
	30	Ring puckering (ip')	100	(8.7)	74	(0.05)	
B_{2u}	31	CH_2 sym. stretch (op, ip')	2883	(100)	2864	(100)	
	32	CH_2 deformation (op, ip')	1493	(0.47)	1466	(1.6)	
	33	CH_2 wag (op, op')	1311	(2.1)	1305	(1.6)	
	34	Ring stretch	1069	(31)	1008	(0.57)	
	35	Ring stretch	1008	(27)	970	(0.02)	
	36	Skeletal bend (op, ip')	367	(0.61)	361	(1.1)	
B_{3u}	37	CH_2 sym. stretch (ip, op')	2881	(8.2)	2860	(43)	
	38	CH_2 deformation (ip, op')	1496	(0.57)	1456	(1.4)	
	39	CH_2 wag (ip, ip')	1375	(8.4)	1316	(0.40)	
	40	Ring stretch	1211	(1.0)	1162	(0.11)	
	41	Ring breathing (op')	864	(20)	877	(0.29)	
	42	Ring bend (ip, op')	785	(7.7)	658	(0.45)	

ip, in-phase; op, out-of-phase.

^a Calculated using the B3LYP/6-311 + +G(d,p) basis set. ^b Calculated relative infrared intensity in parenthesis. Frequency scaled with a scaling factor of 0.985 for frequencies less than 1800 cm⁻¹ and 0.964 for frequencies greater than 2800 cm⁻¹.

^c From Ref. [1].



Fig. 2. Structure of DOBO from the MP2 calculation (MP2/CC-pVTZ).

fairly good but certainly not close to perfect. Table 1 lists the vapor-phase Raman frequencies for DOBO and compares these to the BCO values. The DFT calculated vibrational frequencies and intensities are also listed. The observed and calculated frequencies agree on average within 9 cm⁻¹.

Table 2 lists the Raman inactive vibrations and their DFT calculated frequencies for DOBO. These are also compared to the experimental values of BCO. The frequencies are fairly similar except that the ring modes for DOBO are higher since C–O bond stretching force constants are greater than those for C–C bonds. No experimental data for the infrared active vibrations are shown since there was not enough sample to record the infrared spectra.

Fig. 2 shows the optimized structure for DOBO from the MP2/CC-pVTZ (triple zeta) calculation. The skeletal atoms, unlike the case for BCO which has puckered rings, all lie within a plane resulting in D_{2h} symmetry. The recorded Raman spectrum, which shows only the gerade vibrations, provides further evidence that the molecule has D_{2h} symmetry with a center of symmetry.

6. Conclusions

The vapor-phase Raman spectrum of the DOBO molcules is reported for the first time; it is in excellent agreement with the computed spectrum and this further verifies the molecular structure. Both the Raman spectrum and ab initio calculations show that both of the rings for this bicyclic molecule are planar.

In future work we hope to elucidate the nature of the coupling between the puckering motions of the two rings.

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