

The Microwave Spectrum of Trioxaadamantane¹

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The microwave spectrum of 2,8,9-trioxaadamantane has been investigated in the region from 12.4 to 26.5 GHz. The observed spectrum exhibited the expected symmetric top pattern, with the rotational constant $B_0 = 1848.64$ MHz. Numerous weaker lines were observed and were attributed to vibrational satellites of the main rotational transition. The transitions from $J = 3 \rightarrow 4$ through $J = 6 \rightarrow 7$ were studied and no centrifugal distortion effects were observed.

A structure is derived that is consistent with the observed rotational constants of the normal and one isotopic species by use of the method of diagnostic-least-squares.

The second order Stark effect for the $K = 0$ state yielded a dipole moment of 3.01 ± 0.03 D.

EXPERIMENTAL PROCEDURE

2,8,9-Trioxaadamantane (TOA) is formed by the transesterification of cis-1,3,5-trihydroxycyclohexane with trimethylorthoformate (1,2). Our sample was kindly supplied by Dr. J. G. Verkade of the Iowa State University. The sample was sublimed before using.

The microwave spectrum of TOA was taken on a Hewlett-Packard 8460A microwave spectrometer. Because the crystalline solid had a very low vapor pressure at room temperature (about $50 \mu\text{m}$), slight cooling of the Stark cell to near 0°C caused the vapor pressure to drop so that the spectrum disappeared. Consequently, all spectra were taken at room temperature.

MICROWAVE SPECTRUM

The microwave spectrum of TOA was investigated in the region from 12.4–26.5 GHz. The observed spectrum followed the expected symmetric rotor pattern with no observable centrifugal distortion effects. A number of additional lines were observed on either side of the main line, the strongest being less than 20% as intense. Measurement of these lines revealed that they all followed a symmetric top pattern and were therefore assigned as vibrational satellites. In several cases, the regularly spaced lines of successive excited states could be seen. The transition frequencies and rotational constants along with the rotation–vibration constant, α_v , for these lines are given in Table I.

No spectroscopic investigations have previously been reported for TOA, although the IR, Raman, and microwave spectra of adamantane and some of its derivatives have been

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TABLE I
TRANSITION FREQUENCIES (MHz) OF 2, 8, 9-TRIOXAADAMANTANE
TRANSITION ($J \rightarrow J + 1$)

Line	3 \rightarrow 4	4 \rightarrow 5	5 \rightarrow 6	6 \rightarrow 7	Av rot const	α_c
$\tau = 0$	14789.31	18486.39	22183.66	25880.92	1848.64	—
$\tau' = 1$	14773.56	18466.79	22160.14	25853.48	1846.68	-1.96
$\tau' = 2$	14757.84	18447.30	22136.73	25826.07	1844.72	-3.92
$\tau' = 3$	14741.51	18427.32	22112.27	25797.62	1842.70	-5.94
$\tau'' = 1$	14811.56	18515.00	22217.97	25920.96	1851.50	2.86
$\tau'' = 2$	14839.12	18549.06	22258.82	25968.59	1854.90	6.26
$\tau = 0$ (^{13}C)	14688.04	18361.17	22033.31	25705.59	1836.11	—

$$\alpha_c = B_c - B_0$$

studied (3-5). As would be expected from the rigidity of the cage structure, these show no infrared or Raman active low frequency bands below about 400 cm^{-1} (3).²

A normal coordinate analysis carried out on adamantane by Snyder and Schachtschneider (7) indicates that there are five fundamental vibrational frequencies that lie below 800 cm^{-1} .³ Since these vibrations mainly involve distortions of the heavy-atom framework, it may be expected that these type of vibrations also exist in TOA. Adamantane belongs to the T_d molecular point group and these vibrations belong to the A , E , and T irreducible representations (4). The symmetry of TOA is thought to be C_{3v} . While the molecule must have at least C_3 symmetry in order to give the observed symmetric top spectra, the fact that the adamantane-like cage is known to be remarkably strain-free and rigid leads to the assumption of C_{3v} symmetry. Thus in going from adamantane (T_d) to TOA (C_{3v}), the A , E , and T modes become A and E modes. It was thought that these lower frequency vibrations in TOA could be identified through the l -type doubling phenomena, in which the angular momentum associated with an excited degenerate vibrational state couples with the angular momentum due to overall rotation and gives rise to a splitting of rotational levels (8). Thus vibrational satellites of the degenerate species may be split into multiplets. Although these effects were carefully looked for, none were observed indicating that either the lowest vibrational modes are not degenerate or that the l -type doubling constant is too small to cause observable splittings. Since the splitting increases with J , it may be possible to see this effect at frequencies higher than those studied by us.

STRUCTURE

There are three different isotopic forms of TOA of sufficient natural abundance to give spectra capable of yielding the positions of all of the carbon atoms in the framework. These are labelled α , β , and γ in Fig. 1.

One form results from the replacement of the bridgehead carbon, α , with its ^{13}C isotope. This form is a symmetric top and has a natural abundance of 1.1%. Replacement of

² In fact, the absence of any low frequency vibrational bands in adamantane has led Fateley (6) to propose its use as a pelleting material for far IR spectroscopy of solids.

³ These are: 746 cm^{-1} (A_1), 649 cm^{-1} (T_2), 427 cm^{-1} (E), 423 cm^{-1} (T_2), and 309 cm^{-1} (T_1).

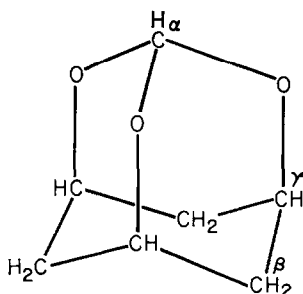


FIG. 1. Trioxaadamantane.

one of the three equivalent secondary carbon atoms, β , by its ^{13}C isotope yields a near symmetric top with a statistical natural abundance of 3.3%. Similarly, a third form, also in 3.3% abundance, results from a substitution at the tertiary carbon position, γ .

An unsuccessful search was undertaken in an attempt to find lines of the two asymmetric ^{13}C species. Under the conditions of high sensitivity required to detect these lines, the region in which they were predicted was found to be obscured by a large number of stronger lines which, as they followed a symmetric rotor pattern, were attributed to high frequency vibrational satellites. Although the near symmetric top forms occurred in 3.3% natural abundance, calculations indicated that when the asymmetry splittings were taken into account, the strongest of the lines would have approximately 0.4% of the intensity of the main line. As noted earlier, a study of the variation of the line intensities as a function of temperature to aid in assigning the spectra was not possible due to the small vapor pressure of the sample. However, the third isotopic species, α , falling in a relatively clear region of the spectra, was successfully assigned.

Due to the limitations on the information available without the asymmetric species, it was decided to combine our experimental quantities with those obtained from other sources and use the technique of diagnostic-least-squares to calculate a structure for TOA (9).

This method systematically varies the values of an initial set of parameters, weighted by their uncertainties, in such a way as to generate a new set of parameters that best reproduce in a least-squares sense the experimentally observed quantities.

It can be seen that the heavy-atom framework can be completely specified in terms of five quantities. These were chosen as follows: bond lengths r_{CO} ⁴ and r_{CC} and bond angles $\angle \text{COC}$, $\angle \text{C}^\beta \text{C}^\gamma \text{C}^\beta$, and $\angle \text{C}^\gamma \text{C}^\beta \text{C}^\gamma$. In addition the C-H distance and $\angle \text{HCH}$ were required to complete the structure.

Since the structure of the cyclohexane ring presumably would not change drastically upon going from adamantane to TOA, the initial values of r_{CC} , $\angle \text{C}^\beta \text{C}^\gamma \text{C}^\beta$, and $\angle \text{C}^\gamma \text{C}^\beta \text{C}^\gamma$ were taken as those of adamantane, as given in the recent electron diffraction work of Hargittai and Hedberg (10). The last two variable parameters, r_{CO} and $\angle \text{COC}$, were chosen based on the values of similar aliphatic oxygen heterocyclic compounds (11). The values of the C-H parameters were also those of Hargittai and Hedberg.

From the observed rotational constant for the ^{13}C species and the use of Kraitichman's equation (12), the distance of the bridgehead atom to the center of mass of the normal

⁴ The $r_{\text{CO}\alpha\text{O}}$ and $r_{\text{CO}\gamma\text{O}}$ distances are assumed equal.

TABLE II
 DIAGNOSTIC LEAST-SQUARES STRUCTURE

Parameter	Initial value	Final value
r_{CO}	$1.43 \pm 0.03 \text{ \AA}^a$	$1.427 \pm 0.007 \text{ \AA}$
r_{CC}	$1.54 \pm 0.01 \text{ \AA}^a$	$1.540 \pm 0.009 \text{ \AA}$
$\angle COC$	112.0 ± 4.0^{ob}	$110.9 \pm 1.2^\circ$
$\angle C^\gamma C^\beta C^\gamma$	108.8 ± 1.0^{ob}	$108.8 \pm 1.0^\circ$
$\angle C^\beta C^\gamma C^\beta$	109.8 ± 1.0^b	$109.8 \pm 1.0^\circ$
r_{CH}	$1.11 \text{ \AA} \text{ (Fixed)}^b$	1.11 \AA
$\angle HCH$	$116.0^\circ \text{ (Fixed)}^b$	116.8°
$\angle OCO$		111.4 ± 1.0^{oc}
$r_{O\alpha-CM}$		1.368 ± 0.005^d

^a Reference 11.

^b Reference 10.

^c Determined by the values of first five parameters.

^d Distance of bridgehead carbon to center of mass from Kraitchman's equation.

species was calculated. This value, in addition to the rotational constant for the normal species, was used in the diagnostic-least-squares calculation.

With r_{CH} and $\angle HCH$ fixed, the five parameters were varied until the set was obtained that reproduced the observations. The initial and final sets of values are shown in Table II, along with additional structural data. In order to investigate the error produced by keeping the methylene hydrogen parameters fixed at their stated values, the structure calculation was repeated for $\angle HCH$ of 123.0° and 109.0° , which are the maximum and minimum values given by the electron diffraction study. Similarly, the same calculation was carried out for r_{CH} of 1.09 \AA and 1.11 \AA . All structures which resulted were within the error limits given in Table II.

DIPOLE MOMENT

The first order stark effect pattern could be readily identified in the higher J transitions for the ground vibrational state and also for several of the stronger satellites.

Because the first order stark effect is very sensitive to errors in the applied electric field, it is not usually used to obtain the dipole moment. The $K = 0$ state of a symmetric top has a second order stark effect, and it thus yields a more accurate value for the dipole moment.

A weak line, found at electric field strengths greater than 1700 V/cm , was identified as the $M = 0$ component of the $K = 0$ state for the $J = 5 \rightarrow 6$ transition, and was used to measure the dipole moment of TOA. Although this stark component for the $J = 6 \rightarrow 7$ transition was stronger and would have yielded a slightly more accurate dipole moment, it could not be measured due to a methanol impurity line that obscured it.

With the stark cell calibrated by using the $J = 1 \rightarrow 2$ transition of OCS and its dipole moment of $0.7152D$ (13), the dipole moment of TOA was found to be $3.01 \pm .03D$.

Although there is no similar molecule whose dipole moment has been measured, TOA can be thought of as being three fused 1, 3-dioxane rings. The dipole moment of 1, 3-dioxane has been determined to be $2.14D$ (14). The dipole moment of TOA could be expected to be roughly 50% larger, which is consistent with the observed value of $3.01D$.

Note added in proof: Bertrand, Compton, and Verkade (*J. Amer. Chem. Soc.* **92**, 2702 (1970)) have measured the dipole moment of TOA in benzene and obtained a value of $3.34 \pm 0.05D$.

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