1 The Pure Rotational Spectrum of a Claisen
2 Rearrangement Precursor Allyl Phenyl Ether Using
3 CP-FTMW Spectroscopy

4 G. S. Grubbs II^{a,*}, Derek S. Frank^b, Daniel A. Obenchain^b, S. A. Cooke^c,
5 Stewart E. Novick^b

6 ^a*Department of Chemistry, Missouri University of Science and Technology, 142 Schrenk*
7 *Hall, 400 W. 11th St., Rolla, MO 65409, U.S.A.*

8 ^b*Department of Chemistry, Wesleyan University, Hall-Atwater Laboratories, 52 Lawn*
9 *Avenue, Middletown, CT 06459-0180, U.S.A.*

10 ^c*Department of Social and Natural Science, Purchase College, State University of New*
11 *York (SUNY), 735 Anderson Hill Road, Purchase, NY 10577, U.S.A.*

12 **Abstract**

The pure rotational spectrum of a Claisen rearrangement precursor, allyl phenyl ether (APE), has been measured on a chirped pulse Fourier transform microwave (CP-FTMW) spectrometer in the 8-14 GHz region. Rotational and centrifugal distortion constants for multiple conformations have been determined and are reported for the first time. This is the first study of a phenyl-containing ether where multiple conformers were experimentally observed all within their ground vibrational states. Quantum chemical calculations have been performed to isolate low energy geometries of APE and are implemented to aid in spectral assignment. Other structural parameters such as planar moments and inertial defects for the allyl phenyl ether conformers are presented and compared to similar molecules for discussion.

13 *Keywords:* Allyl Phenyl Ether, Chirped Pulse, Rotational Spectroscopy,
14 Quantum Chemistry

*Corresponding Author. E-mail: grubbsg@mst.edu

March 25, 2016

URL: <http://openscholar.purchase.edu/cooke/> (S. A. Cooke),
<http://snovick.faculty.wesleyan.edu/> (Stewart E. Novick)

Preprint submitted to Journal of Molecular Spectroscopy

15 1. Introduction

16 In 1912, Claisen reported the discovery of an ether undergoing rearrange-
17 ment to an alcohol upon the addition of heat.[1] The Claisen rearrangement
18 is now the basis for many reaction processes and is commonly taught in
19 undergraduate organic chemistry lecture and laboratory courses.

20 One basic Claisen rearrangement ether, allyl phenyl ether, becomes 2-
21 allylphenol according to the mechanism in Figure 1. Inspection of Figure 1
22 shows that the $-\text{CH}_2$ group must be in the vicinity of *ortho* carbon of the
23 ring. Since the addition of heat has long been known to be the driving force
24 of the reaction, it is important to understand if this requirement is due to
25 lower energy conformations of the species being more readily populated. The
26 authors, therefore, set out to monitor the $-\text{CH}_2$ carbon-to-*ortho* carbon dis-
27 tances using rotational spectroscopic techniques on the possible conformers
28 of allyl phenyl ether present in a molecular beam. CP-FTMW techniques
29 have the added benefit of quickly obtaining spectra with correct relative
30 intensities,[2] thus allowing for easy determination of any new species in the
31 sample.

32 Another motivation for the study of allyl phenyl ether is interstellar.
33 Smaller aromatic molecules are of interest to the interstellar community due
34 to the large predicted abundance of polycyclic aromatic hydrocarbons (PAH).[3]
35 PAH molecules, in turn, have recently been of interest in both the interstellar
36 medium and that of planetary and planetary satellite atmospheres.[4] Small,
37 stable aromatic systems are important in understanding how chemistry takes
38 place in the far reaches of the galaxy and can provide links to other molecules
39 already discovered.[3, 4]

40 In addition to structural analysis for chemical reactivity and interstellar
41 motivations, ethers have also previously been shown to have free rotor inter-
42 nal rotation and multiple low-lying energy conformations.[3, 4, 5, 6, 7, 8, 9]
43 These types of complexities, along with the typical sizeable dipole moments
44 and high vapor pressures exhibited by simple ethers, make them generally
45 well suited for chirped pulse rotational studies.[6, 9, 10, 11] The chirped pulse
46 spectra allow for reliable transition intensities which are of great assistance
47 in assigning dense spectra from multiple conformations while still providing
48 the isotopic resolution useful in structural analysis.[2]

49 In this work, we present the first observed rotational spectrum and anal-
50 ysis of the two lowest energy conformers for the Claisen rearrangement pre-
51 cursor, allyl phenyl ether. The results are compared to quantum chemical
52 optimized structures and experimental results of similar phenyl-containing
53 molecules to aid in understanding of the experimental structure.

54 2. Experiment

55 All measurements were made at Wesleyan University. 99% allyl phenyl
56 ether (APE) was purchased from Sigma-Aldrich® and used without further
57 purification. The sample was placed in a “U”-shaped tube where approxi-
58 mately 2 atm of argon was allowed to pass over the liquid sample approxi-
59 mately 40 cm upstream of a Parker-Hannifin™ Series 9 solenoid valve with
60 0.8 mm orifice. The Ar/APE gas mixture is supersonically expanded into a
61 vacuum chamber held at 10^{-9} atm. The expansion cools the molecules to a
62 rotational temperature of ≈ 4 K. The sample was investigated on a chirped-
63 pulse, Fourier transform (CP-FTMW) spectrometer in the 8-14 GHz range.

64 A sample of the resultant spectrum is shown in Figure 2. This instrument
 65 has been described in detail elsewhere [2, 12] and is based upon the chirp
 66 pulse experiment previously introduced by Pate and coworkers [13, 14, 15].
 67 Briefly, the instrument mixes a microwave pulse of frequency ν with a fast (5
 68 μ s) linear frequency sweep of DC-1 GHz generating a $\nu \pm 1$ GHz broadband
 69 pulse. The pulse is then amplified using a 5 Watt solid state amplifier and
 70 broadcast onto the gas sample through a horn antenna. The radiation is
 71 then turned off and a second antenna horn receives a free induction decay
 72 (FID) signal generated by the decohering molecular ensemble. The signal
 73 is then passed through an amplification stage and then proceeds to be di-
 74 rectly digitized on a 12 GHz, 40 GS/s oscilloscope (TektronixTM TDS6124
 75 Digital Oscilloscope). 30,000 signal averages were acquired for APE with an
 76 uncertainty of 10 kHz attributed to line centers.

77 3. Quantum Chemical Calculations

78 APE conformations were calculated using the Gaussian09 software suite.[16]
 79 Possible minimum energy structures were identified by first doing a gener-
 80 alized geometry calculation and then performing a complete rotation of the
 81 O-C-C=O and C-O-C-C dihedral angles. A secondary geometry optimiza-
 82 tion was then performed using starting points geometries from wells found
 83 during these scans to obtain more accurate equilibrium structures. All struc-
 84 tures were optimized using a MP2 level of theory with a 6-311G++(3d,2p)
 85 basis set. The four lowest found, optimized structures of APE are given in
 86 Figure 3. The two lowest energy structures of APE shown in the *ab*-, *bc*-, and
 87 *ac*-planes in Figure 4. The structural parameters for all APE conformers are

summarized in Table 1 with 2-allylphenol given for comparison. As can be seen in the figures, the lowest two energy conformations of APE have a heavy atom backbone structure that lies mainly in the *ab*-plane. This heavy atom backbone structure is shown explicitly by the small P_{cc} values calculated for both APE Conf. 1 and 2 at 10.1 and 1.60 $\mu\text{\AA}^2$, respectively. However, these slight differences in structure give rise to a large shift in dipole moment orientation with μ_a being the largest in Conf. 1 to μ_b being the largest in Conf. 2. The switch in dipole magnitude was useful when making transition assignments to specific conformations and will be commented on later in the text.

4. Results and Analysis

As shown in Figure 2, it was immediately apparent that multiple species were present in the collected frequency range. Sixty-one transitions of Conf. 1 and forty-one transitions of Conf. 2 were observed in the spectra. The observed spectra for Conf. 1 consisted of *a*-type, *R*-branch as well as *b*-type, *R*- and *Q*-branch transitions. The *a*-type, *R*-branch transitions, however, were of the strongest intensity as a whole, reinforcing the equilibrium structure calculated dipole moment values. Conf. 2 transitions also consisted of *a*-type, *R*-branch and *b*-type, *R*- and *Q*-branch transitions. These transitions, however, had a different intensity profile with the most intense transitions belonging to *b*-type spectra, again reinforcing the equilibrium structure calculated dipole moments for the conformers. No *c*-type spectra were observed which was also consistent with the predicted μ_c dipole moments of the conformers. Attempts were made to assign the ^{13}C isotopologue, but there was

112 not enough information for a suitable fit. Also, there were no transitions
113 attributed to that of 2-Allylphenol in the spectra. Transition assignments
114 for both species can be found in the Supplemental Data.

115 Assignment of the spectra were made using Pickett’s SPFIT/SPCAT suite
116 of programs.[17] Spectroscopic parameters can be found in Table 2. To assist
117 in this process, the graphical front-end Assignment and Analysis of Broad-
118 band Spectra (AABS) package,[18] available from Kisiel on the PROSPE
119 website,[19] was used. The authors made use of the fact that the major
120 dipole moment axis switched orientation as this provides different patterns
121 of the most intense spectra.[20] This pattern recognition method was uti-
122 lized heavily in the early stages of transition assignment to ease the burden
123 of knowing the rotational constants to high degrees of accuracy. Watson’s A-
124 type reduced Hamiltonian[21] in the I^r representation was used in the fitting
125 of spectra. Only the rigid rotor and quartic centrifugal distortion constants
126 were needed for a suitable fit of Conf. 1 while rigid rotor, quartic, and sextic
127 terms were needed for Conf. 2. Although other centrifugal distortion terms
128 for each species were attempted, including the δ_J quartic term, these con-
129 stants were indeterminable and, thus, left out of the fit. Both fits, however,
130 are well within the attributed experimental uncertainty of 10 kHz mentioned
131 in the *Experiment* section. Quality of the fits including obs-calc values for
132 each assigned transition are also found in the Supplemental Data.

133 5. Discussion

134 A comparison of the experimental and calculated parameters in Tables 2
135 and 1 show that there is excellent quantitative agreement between the calcu-

lated equilibrium structures and the experimental ground state structure for both conformers. Since the calculated equilibrium structures of Conformers 1 and 2 proved to be very close to the experimental structure, they will be utilized for visual aids when providing quantitative structural content later in this section.

As a secondary confirmation of the calculated and experimental agreement, second moments, moments of inertia, inertial defects, and Ray’s asymmetry parameters for the experimental parameters are shown in Table 3[22, 23] along with similar experimentally determined molecular structures. This is the first study of a phenyl-containing ether where multiple conformers were experimentally observed all within their ground vibrational states.[3, 4, 6, 7, 8] Even though there is little heavy-element isotopologue information present for the family of known molecules (only anisole has ^{13}C and ^{18}O assigned spectra[3]),[3, 4, 6, 7, 8] the second moment information provides useful insight into the experimental structure.[24, 25]

Bohn’s work on interpreting second moments[24] involves breaking functional groups into generalized second moment contributions. This is especially useful for comparisons across a family or system of similar molecules when trying to understand the effects of adding, removing, or complexing separate subunits when isotopic substitution spectra and/or analyses are unavailable.[25] The comparisons may be between two separate second moment values, say P_{aa} and P_{bb} , but the contributions remain very similar for each functional group (phenyl group, $-\text{CH}_2$, $-\text{CH}_3$, etc.). As mentioned earlier, this is the first reported measurement of a phenyl-containing ether with multiple experimentally observed conformers in the ground state. To un-

161 derstand how these structures compared to other experimentally determined
 162 species in the family, we will start with the simplest ether of the family,
 163 anisole, and "build up" with general values from Ref. [24].

164 From Refs. [3] and [6], the ground vibrational state structure lies pre-
 165 dominately in the *ab*-plane with the hydrogens of the anisole out-of-plane.
 166 According to Bohn[24], the phenyl group, -C₆H₅, should contribute 89.2 uÅ²
 167 to P_{bb} and the methyl group, -CH₃, should contribute 1.6 uÅ², giving 90.8
 168 uÅ². This means the remaining amount of 8 uÅ² needed to get to the 98.8
 169 uÅ² reported in Ref. [6] can be attributed to the oxygen atom in the ether.
 170 The addition of a second methyl group to create phenetole increases the P_{bb}
 171 by 1.6 uÅ² in the model and the approximation becomes 100.4 uÅ². The
 172 experimental value for phenetole is 100.7 uÅ² suggesting that it is adding
 173 this mass off of the *b*-axis (as expected). If we go one step further and add
 174 a -CH₂ to make the allyl (instead of a methyl) to this structure, we arrive
 175 at 102 uÅ², very close to the lowest energy conformer P_{bb} of 101.2 uÅ² mea-
 176 sured for APE. This, however, is not taking into account the slight out of
 177 plane contribution provided by the addition of the allyl species. If we were
 178 adding strictly in the *ab*-plane, this would have been easily monitored by an
 179 approximate jump of 1.6 uÅ² in the P_{cc} value, but there is approximately 6
 180 uÅ² difference between Phenetole and APE Conf. 1 in P_{cc} meaning a signifi-
 181 cant amount of mass is no longer *ab*-planar, but now adding along the *c*-axis.
 182 This is shown in Figure 4 for Conf. 1 where the O-C-C-C chain of the allyl
 183 species is being distributed in the *ac*-plane also causing the phenyl group to
 184 be slightly distributed along the *c*-axis as well which accounts for the small
 185 discrepancy in our assumption versus the measured value.

186 Since there are no direct experimental comparable species to understand
 187 Conf. 2, we must start with the calculated equilibrium geometries. Looking
 188 at Figure 4 for Conf. 2 it is noticed that the calculated equilibrium structure
 189 is completely *ab*-planar. In Bohn’s work on Benzyl alcohol, he mentions that
 190 P_{cc} should be $1.6 \text{ u}\text{\AA}^2$ if heavy-atom planar.[24] This P_{cc} value should still
 191 hold even with the addition of carbon-containing groups, so long as all heavy
 192 atoms are still in-plane. This is very close to the measured P_{cc} value of 1.9
 193 $\text{u}\text{\AA}^2$ confirming the planar structure. The inertial defect also confirms heavy
 194 atom-planar structure as anisole, found through isotopic substitution to have
 195 the heavy-atoms in the *ab*-plane[3] shares a very similar value in its inertial
 196 defect as Conf. 2 ($-3.40940(2)$ [3, 6] vs. $-3.971(1)$, respectively). Anisole, just
 197 like APE Conf. 2, has only two hydrogens out-of-plane in the calculated
 198 structure. Similarly, completely *ab*-planar 1-Phenyl-1-butyne-3-ene has an
 199 inertial defect of -0.41 , but has no hydrogens out-of-plane.

200 From the *Introduction*, one original goal of this study was to monitor
 201 the $-\text{CH}_2$ carbon-to-*ortho* carbon distance to provide an explanation as to
 202 why heat is needed for the Claisen rearrangement. Since it has already been
 203 determined that the lowest two energy conformers of the quantum chemical
 204 calculations are very similar to the experimentally determined structures, we
 205 will use these calculated distances for comparison. For Conf. 1 this distance
 206 is $5.21 \text{ \AA}$ for the nearest *ortho* carbon and for Conf. 2 this distance is $4.85 \text{ \AA}$ for
 207 the nearest *ortho* carbon. Both of these are very large distances compared
 208 to $3.59 \text{ \AA}$ and $4.57 \text{ \AA}$ for Conf. 3 and Conf. 4, respectively. Conf. 3 and Conf.
 209 4, however are also much higher in energy at 633.0 cm^{-1} and 714.4 cm^{-1} ,
 210 respectively. Again, in our experiment, only the two lowest energy conformers

211 were observed with no observation of 2-allylphenol in the spectra. From this
212 and the Claisen mechanism requiring proximity between the -CH₂ and *ortho*
213 carbons to start the mechanism, it can be concluded that the rearrangement
214 has been precluded in our experiment due to structural reasons and that heat
215 is needed, at least in part, to access structural conformers that are higher in
216 energy to begin the reaction.

217 6. Conclusion

218 The microwave spectrum of APE has been collected and analyzed for
219 the first time. Rotational and centrifugal distortion constants have been de-
220 termined and reported. Quantum chemical calculations were made of the
221 molecular structures and are in good agreement with the determined ro-
222 tational constants from experiment. Comparisons of the second moments
223 found for both conformers in this work with those in similar molecules have
224 been used in conjunction with the quantum chemical calculations in under-
225 standing the experimental structures. Conf. 1 has been determined to be
226 very similar in structure to that of predecessors anisole and phenetole but
227 with the O-C-C-C chain and phenyl group being slightly out of the *ab*-plane.
228 Conf. 2, through its P_{cc} value, has been determined to be almost completely
229 *ab*-planar with the exception of 2 out-of-plane hydrogens much like that of
230 anisole. For the lowest two energy conformers it has been determined that
231 the Claisen rearrangement is precluded for structural reasons.

232 7. Acknowledgements

233 The authors acknowledge the financial support of the NSF, grant CHE-
234 1011214. We also thank Wesleyan University for computational resources
235 supported by the NSF under grant number CNS-0619508. GSGII recognizes
236 a University of Missouri Research Board Grant for financial support. GSGII
237 would also like to acknowledge Bob Bohn for his pioneering work with struc-
238 tural second moment analysis which made most of the insights in this work
239 possible.

240 **References**

- 241 [1] L. Claisen, Chem. Ber. 45 (1912) 3157.
- 242 [2] G. S. Grubbs II, C. T. Dewberry, K. C. Etchison, K. E. Kerr, S. A.
243 Cooke, Rev. Scient. Instrum. 78 (2007) 096106.
- 244 [3] O. Desyatnyk, L. Pszczółkowski, S. Thorwirth, T. M. Krygowski,
245 Z. Kisiel, Phys. Chem. Chem. Phys. 7 (2005) 1708.
- 246 [4] J. A. Sebree, D. F. Plusquellic, T. S. Zwier, J. Mol. Spectrosc. 270 (2011)
247 98.
- 248 [5] D. G. Lister, J. Mol. Struct. 68 (1980) 33.
- 249 [6] B. Reinhold, I. A. Finneran, S. T. Shipman, J. Mol. Spectrosc. 270
250 (2011) 89.
- 251 [7] L. Ferres, W. Stahl, H. V. L. Nguyen, Microwave spectroscopic and
252 quantum chemical investigations on phenyl formate and phenetole, The
253 24th Colloquium on High Resolution Molecular Spectroscopy, 2015.
- 254 [8] L. Ferres, W. Stahl, H. V. L. Nguyen, Mol. Phys. Manuscript Submitted.
- 255 [9] B. E. Long, G. S. Grubbs II, S. A. Cooke, The pure rotational spectra
256 of the two lowest energy conformers of *n*-butyl ethyl ether, *66th Inter-*
257 *national Symposium on Molecular Spectroscopy*, 2011, **RH13**.
- 258 [10] G. S. Grubbs II, S. A. Cooke 115 (2011) 1086.
- 259 [11] G. S. Grubbs II, S. A. Cooke, Chem. Phys. Lett. 495 (2010) 182.

- 260 [12] G. S. Grubbs II, R. A. Powoski, D. Jojola, S. A. Cooke, J. Phys. Chem. A
261 114 (2010) 8009.
- 262 [13] G. G. Brown, B. C. Dian, K. O. Douglass, S. M. Geyer, B. H. Pate, J.
263 Mol. Spectrosc. 238 (2006) 200.
- 264 [14] B. C. Dian, G. G. Brown, K. O. Douglass, B. H. Pate, Science 320 (2008)
265 924.
- 266 [15] G. G. Brown, B. C. Dian, K. O. Douglass, S. M. Geyer, S. T. Shipman,
267 B. H. Pate, Rev. Scient. Instrum. 79 (2008) 053103.
- 268 [16] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel,
269 G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone,
270 B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.
271 P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg,
272 M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T.
273 Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery,
274 Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N.
275 Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari,
276 A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.
277 M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J.
278 Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R.
279 Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V.
280 G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich,
281 A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and
282 D. J. Fox, Gaussian 09, Gaussian, Inc., 340 Quinnipiac Street, Building
283 40, Wallingford, CT, 06492, 2009, copyright © 1994-2009.

- 284 [17] H. M. Pickett, J. Mol. Spectrosc. 148 (1991) 371.
- 285 [18] Z. Kisiel, L. Pszczolkowski, I. R. Medvedev, M. Winnewisser, F. C. D.
286 Lucia, C. E. Herbst, J. Mol. Spectrosc. 233 (2005) 231.
- 287 [19] Z. Kisiel, PROSPE – Programs for ROtational SPEctroscopy, URL:
288 <http://info.ifpan.edu.pl/kisiel/prospe.htm>.
- 289 [20] S. A. Cooke, P. Ohring, Journal of Spectroscopy 2013 (2013) Article ID
290 698392.
- 291 [21] J. K. G. Watson, Vibrational Spectra and Structure 6 (1977) 1.
- 292 [22] C. H. Townes, A. L. Schawlow, Microwave Spectroscopy, Dover Publi-
293 cations, Inc., New York, 1975.
- 294 [23] W. Gordy, R. L. Cook, Microwave Molecular Spectra; Techniques of
295 Chemistry Vol. XVIII, Wiley, New York, 1984.
- 296 [24] R. K. Bohn, J. A. Montgomery, Jr., H. H. Michels, J. Byrd, Second
297 moments (planar moments) and their application in spectroscopy., The
298 Ohio State University 68th International Symposium on Molecular Spec-
299 troscopy, 2013, wH03.
- 300 [25] G. S. Grubbs II, D. A. Obenchain, D. S. Frank, S. E. Novick, S. A.
301 Cooke, A. Serrato III, W. Lin, J. Phys. Chem. A 119 (2015) 10475.

Table 1: Calculated^a Rotational Constants, Second Moments, and Dipole Moments of Allyl Phenyl Ether and 2-Allylphenol.

Parameter	APE Conf. 1	APE Conf. 2	APE Conf. 3	APE Conf. 4	2-Allylphenol
A /MHz	4539.7	4193.8	2825.8	3419.5	2511.4
B /MHz	631.8	693.3	868.4	739.9	1008.0
C /MHz	567.2	597.2	718.2	664.2	795.4
ΔE /cm ⁻¹	0	63.3	633.0	714.4	
P_{aa} / $\mu\text{\AA}^2$	789.8	727.3	553.4	648.1	467.8
P_{bb} / $\mu\text{\AA}^2$	101.2	118.9	151.0	112.8	167.6
P_{cc} / $\mu\text{\AA}^2$	10.1	1.60	28.6	35.0	33.6
$ \mu_a $ /Debye	1.14	0.32	1.13	0.90	1.26
$ \mu_b $ /Debye	0.52	1.14	0.88	0.91	0.90
$ \mu_c $ /Debye	0.18	0.00	0.10	0.26	0.43

^a All calculations were performed at MP2/6-311G++(3d,2p) level of theory.

Table 2: Spectroscopic Parameters of Allyl Phenyl Ether.

Parameter	Conformer 1	Conformer 2
A / MHz	4565.112(2) ^a	4181.703(5)
B / MHz	629.1454(1)	692.3752(8)
C / MHz	564.6316(1)	596.7368(8)
Δ_J / kHz	0.0176(7)	0.03(1)
Δ_{JK} / kHz	-0.124(7)	-0.10(2)
Δ_K / kHz	4.5(5)	-3(1)
δ_K / kHz	—	0.4(1)
Φ_J / mHz	—	54.(34)
N^b	61	41
Microwave RMS ^c / kHz	4.5	7.6

^a Numbers in parentheses give standard errors

(1σ , 67% confidence level) in units of the least significant figure.

^b Number of observed transitions used in the fit.

^c Microwave RMS is defined as $\sqrt{\left(\sum \left[(\text{obs} - \text{calc})^2\right] / N_{\text{lines}}\right)}$

Table 3: Structural Parameters for a Series of Similar Phenyl-Containing Molecules.

Parameter	Anisole ^a	Phenetole ^b	1-Phenyl-1-butyne-3-ene ^c	APE Conf. 1 ^d	APE Conf. 2 ^d
$P_{aa} / \text{u}\text{\AA}^2$	320.323152(9) ^e	544.00956(2)	880.87(1)	793.8168(1)	727.9851(7)
$P_{bb} / \text{u}\text{\AA}^2$	98.791362(9)	100.72772(2)	101.72(1)	101.2429(1)	118.9192(7)
$P_{cc} / \text{u}\text{\AA}^2$	1.704699(9)	3.35887(2)	0.21(1)	9.4617(1)	1.9355(7)
$I_a / \text{u}\text{\AA}^2$	100.496061(4)	104.086586(3)	101.9287(6)	110.70462(5)	120.8548(1)
$I_b / \text{u}\text{\AA}^2$	322.02785(1)	547.36843(2)	881.08(2)	803.2786(1)	729.9207(8)
$I_c / \text{u}\text{\AA}^2$	419.11451(1)	644.73727(3)	982.59(2)	895.0597(2)	846.904(1)
$\Delta / \text{u}\text{\AA}^{2,f}$	-3.40940(2)	-6.71774(4)	-0.41(2)	-18.9234(2)	-3.871(1)
κ	-0.809816	-0.931507	-0.97	-0.9677	-0.947

^a Combined fit of Ref. [6] and [3] from Ref. [6].

^b From Ref. [7] and [8].

^c From Ref. [4].

^d This work.

^e Numbers in parentheses give standard errors (1σ , 67% confidence level) in units of the least significant figure.

^f Inertial Defect $\Delta = I_c - I_a - I_b$

Figure 1: Claisen rearrangement mechanism of Allyl Phenyl Ether to 2-Allylphenol.

Figure 2: Top portion: Sample spectrum of APE from 12000 MHz to 12300 MHz.

Figure 3: Top portion: Calculated equilibrium structures of the four APE conformers.

Figure 4: Top portion: Calculated equilibrium structures of the lowest two energy conformers of APE in the ab -, bc -, and ac -planes.