Microwave survey of the conformational landscape exhibited by the propeller molecule triethyl amine

Ha Vinh Lam Nguyen, Raphaela Kannengiesser, Wolfgang Stahl

PCCP

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

ARTICLE TYPE

Microwave survey of the conformational landscape exhibited by the propeller molecule triethyl amine

Ha Vinh Lam Nguyen,* Raphaela Kannengießer, and Wolfgang Stahl[a]

Conformational studies with quantum chemical methods yielded for the most stable conformer of triethyl amine a propeller-like structure belonging to the point group C_3, which corresponds to an oblate top. The microwave spectrum of this conformer with ^{14}N hyperfine splitting of all rotational transitions was assigned and molecular parameters were determined. The rotational constants were found to be $A = B = 2.314873978(11)$ GHz, the ^{14}N quadrupole coupling constant $\chi_{cc} = -5.2444(07)$ MHz. The observed spectrum could be
10 reproduced within experimental accuracy. The standard deviation of a global fit with 43 rotational transitions is 1.5 kHz. The propeller-like structure seems to be energetic favorable and therefore also typical for related systems like triethyl phosphine, triisopropyl amine, tri-n-propyl amine, and tri-*tert*-butyl amine. Furthermore, the rotational transitions of two isotopologues, $^{13}C_2$ and $^{13}C_5$, could be measured in natural abundance and fitted with an excellent standard deviation. The C rotational constants could be determined to be 1.32681(96) GHz and 1.32989(18) GHz for the $^{13}C_2$ and $^{13}C_5$ isotopologues, respectively.

15
1. Introduction

Amines are important derivates of ammonia, where one or more protons are replaced by organic substituents. Small aliphatic amines are often used in the pharmaceutical and fertilizer
20 industry, or as solvents. Many studies on ammonia[1] and its derivates have been carried out in the microwave region. In our investigation on diethyl amine,[2] where two protons in ammonia are substituted by ethyl groups, three different effects influenced the spectrum. The quadrupole hyperfine splittings due to the
25 nuclear spin of $I = 1$ of the ^{14}N nucleus and the splittings due to the internal rotation of the two equivalent methyl groups could be resolved. The barrier to internal rotation has been determined to be 1051 cm^{-1}. This motivated us to study triethyl amine, a related molecule, where all the protons in ammonia are substituted by
30 ethyl groups. We were interested in comparing the ^{14}N quadrupole coupling constants of this molecule with ammonia, diethyl amine, and other molecules like trimethyl amine,[3] quinuclidine,[4] and nitrogen trifluoride.[5] It is also interesting to find out whether the barrier to internal rotation changes, i.e.
35 whether splittings of three internal rotors can be observed.

By rotating the ethyl groups, a large number of different geometries of triethyl amine can be generated. To find out which of those geometries are stable conformers, which conformers can be observed under molecular beam conditions, and which
40 symmetry the most stable conformer has, a combination of molecular beam Fourier transform microwave (MB-FTMW) spectroscopy and quantum chemical calculations were carried out. Furthermore, we were interested in a comparative quantum chemical study of related molecules such as triethyl phosphine,
45 triisopropyl amine, tri-n-propyl amine, and tri-*tert*-butyl amine.

2. Experimental setup

All spectra were recorded using a MB-FTMW spectrometer which is a modified version of the spectrometer described in ref. [6] and [7]. Transitions within the frequency range from 4 to 26.5 GHz
50 can be recorded. Triethyl amine was obtained from Merck

Schuchardt, Hohenbrunn, Germany. A mixture of triethyl amine with helium at a concentration of 1% by volume and a total pressure of 100 kPa was used throughout.

The spectrometer can be used both in the high resolution mode
55 and in the scan mode. In the scan mode overlapping spectra in a grid of 0.25 MHz were recorded to give the broadband scans where only the line positions are indicated. In the high resolution mode, all lines split into doublets due to the Doppler effect. All lines were rather strong. For most transitions we found a line
60 width in the range from 20 to 25 kHz. This enabled us to determine transition frequencies with an accuracy of approximately 2 kHz.

3. Quantum chemical calculations

3.1 Triethyl amine

65 #### 3.1.1 Optimization

Triethyl amine is a molecule with 22 atoms, which is too large for a classical structure determination by isotopic substitution. Quite a big number of geometries is possible, but not all of them are stable conformers. Quantum chemistry is a helpful method for
70 calculating the conformers as well as for giving reasonable starting values of rotational constants to assign the microwave spectrum.

In total, 216 different starting geometries were calculated using the program *Gaussian09* [8] by varying the three dihedral
75 angles $\alpha_1 = \angle(C_{16}, N, C_2, C_5)$, $\alpha_2 = \angle(C_{16}, N, C_9, C_{12})$, and $\alpha_3 = \angle(C_9, N, C_{16}, C_{19})$, in each case from $-120°$ to $180°$ in a grid of $60°$. Atom numbers are given in Figure 1. The MP2 method and the basis set 6-311++G(d,p) were used, since it turned out to be reliable in many other molecules studied before.[9-11]
80 From 216 starting geometries, only 8 conformers were found. The frequency calculation for conformer VIII yielded an imaginary frequency, i.e. this conformer is a saddle point. All other conformers are stable; they are indicated in Figure 2 in order of their relative energies. Their energy values, dipole
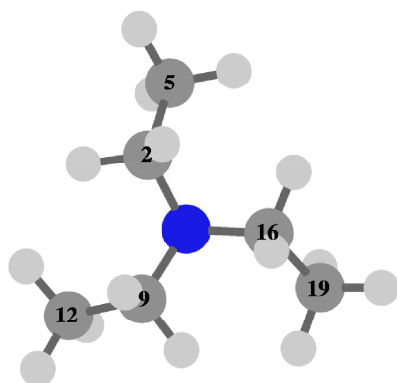
Fig. 1 Geometry of the observed conformer (most stable) of triethyl amine. Only C atoms are labeled.

moments, and rotational constants are given in Table 1. The
5 nuclear coordinates in the principal axes system of 7 stable
conformers are available as supplementary material in Table S-1.
It should be noted that conformers I, II, III, and VII each have an
enantiomeric partner, whereas conformers IV and V have a
structure with no possible enantiomeric partner.

10

Table 1. The energy values, dipole moments, and rotational constants
of 7 stable conformers of triethyl amine.

Conf.	rel. E kJ/mol	μ_a /D	μ_b /D	μ_c /D	A /GHz	B /GHz	C /GHz
I	11.6310	0.330	0.264	0.577	3.044	2.010	1.519
II	3.0817	0.261	0.367	0.650	2.931	2.016	1.373
III	0.0000	0.000	0.000	0.781	2.319	2.319	1.326
IV	2.2143	0.000	0.416	0.643	3.387	1.855	1.407
V	3.2028	0.000	0.303	0.739	3.114	1.941	1.348
VI	8.2523	0.560	0.109	0.655	2.956	1.993	1.364
VII	22.5982	0.000	0.000	0.488	2.405	2.405	1.754

Conformer III is the most stable one with a C_3 symmetric,
propeller-like structure (see also Figure 1). The methyl groups are
all tilted in the direction of the free electron pair on the nitrogen
15 atom by the same angle $\angle(C_5, C_2, N) = \angle(C_{19}, C_{16}, N) = \angle(C_{12}, C_9, N)$ of 112.5 °. The A and B rotational constants are identical
and a dipole moment exists only in the c direction. Triethyl amine
is consequently an oblate top. Conformer VII is likewise an
oblate top. In this case, the methyl groups are tilted away from
20 the free electron pair. However, this conformer has an energy
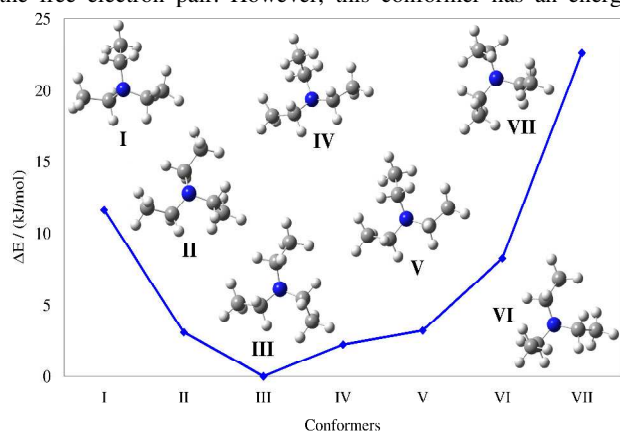
Fig. 2 Stable conformers of triethyl amine calculated at the MP2/6-
311++G(d,p) level. The energy values are relative to the most stable
conformer III (−291.559737 Hartree). Only one enantiomer of conformers
25 I, II, III and VII is indicated.
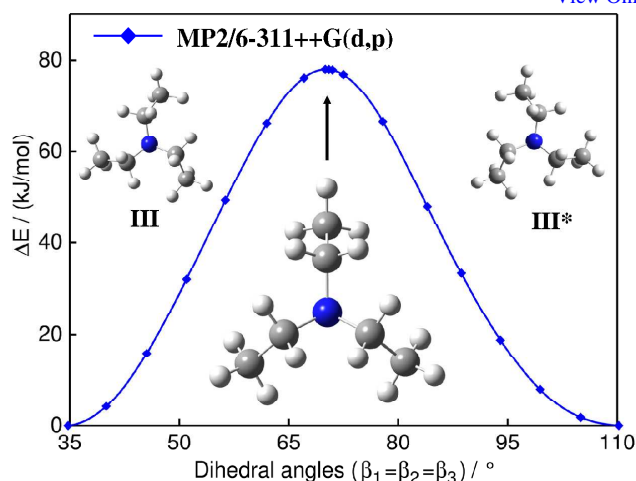
Fig. 3 The potential energy curve obtained by varying the dihedral angles
$\beta_1 = \angle(C_2, N, C_{19}, C_{16})$, $\beta_2 = \angle(C_9, N, C_5, C_2)$, and $\beta_3 = \angle(C_{16}, N, C_{12}, C_9)$
and keeping the dihedral angle $\beta_4 = \angle(C_5, C_{12}, C_{19}, N)$ fixed.

30 value 22.6 kJ/mol higher than that of conformer III and is
unlikely to be observed under molecular beam conditions.

As mentioned before, the most stable conformer III appears as
an enantiomeric pair. The propeller-like structure can have a
clockwise or anti-clockwise direction. To find out, whether a
35 tunneling process between the two enantiomers is possible,
calculations to determine the transition state were carried out.
Three dihedral angles $\beta_1 = \angle(C_2, N, C_{19}, C_{16})$, $\beta_2 = \angle(C_9, N, C_5, C_2)$, and $\beta_3 = \angle(C_{16}, N, C_{12}, C_9)$, which are all 34.77° and 110.24°
in conformer III and its enantiomer III*, respectively, were kept
40 fixed whereas other molecular parameters were allowed to relax.
Assuming that these angles vary continuously in the same way,
β_1, β_2, and β_3 were varied from 34.77° to 110.24° in a grid of
10.78°. In addition, a further dihedral angle $\beta_4 = \angle(C_5, C_{12}, C_{19}, N)$ has to be fixed at 17.84° in all calculations to keep the
45 distance between the nitrogen atom and the C_5-C_{12}-C_{19} plane
constant. This value was found in both conformer III and III*.
The energy curve is given in Figure 3. Some additional
calculations were carried out to have a better parameterization.
The Fourier coefficients are available as supplementary material
50 (Table S-2). The energy maximum is expected to be at about
70.5°.

We assumed that the transition state should have an exact C_{3v}
structure since the three ethyl groups are equivalent. Taking this
constraint, we created a C_{3v} starting geometry by rotating one of
55 the ethyl groups of the structure at the maximum
($\beta_1 = \beta_2 = \beta_3 = 70.5°$) by 120° and 240°. A full optimization of
this C_{3v} starting geometry to a minimum retained the C_{3v} structure
indicated in Figure 4. A frequency calculation showed three
imaginary frequencies, which correspond to the deformation of
60 the three ethyl groups from conformer III to conformer III*. The
tunneling barrier between the two enantiomers is approximately
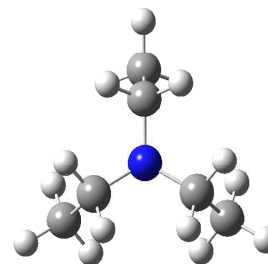
Fig. 4 Geometry of the transition state of triethyl amine with a C_{3v}
symmetry.

Table 2. Parameters describing the overall rotation and ^{14}N quadrupole coupling of triethyl amine as well as its $^{13}C_2$ and $^{13}C_5$ isotopologues fitted with the program *spfit*.

Parameter	Unit	Main isotopologue	Calc.	$^{13}C_2$ isotopologue	$^{13}C_5$ isotopologue
A	GHz	2.314873978(11)[a]	2.3194[b]	2.31293315(34)	2.31302815(28)
B	GHz	2.314873978(11)	2.3191[b]	2.29283301(33)	2.25126785(40)
C	GHz	1.3262 (fixed)	1.3262[b]	1.32681(96)	1.32989(18)
D_J	kHz	0.9619(17)		0.9694(88)	1.369(14)
D_{JK}	kHz	−1.5885(43)		−3.594(27)	1.988(25)
χ_{cc}	MHz	−5.2444(07)	−5.2425[c]	−5.2660(40)	−5.947(98)
$\chi_{bb} - \chi_{aa}$	MHz	0.0[d]			−0.257(19)
N		43		16	10
σ	kHz	1.5		0.5	0.4

[a] Parameters are given with one standard uncertainty in parentheses.
[b] Calculated at the MP2/6-311++G(d,p) level.
[c] Structure optimization at the MP2/6-311+G(df,pd) level, electric field gradient calculation at the B3PW91/6-311+G(d,p) level (see text).
[d] Due to symmetry.

27 kJ/mol. Due to the high barrier, we conclude that a splitting due to an enantiomer tunneling process cannot be observed under molecular beam conditions. It should be noted that the energy of the transition state is much lower than the energy of about 80 kJ/mol found for the maximum at 70.5°, since the structures are different, as indicated in Figure S-1 in supplementary material. The Cartesian coordinates of the transition state are given in Table S-3.
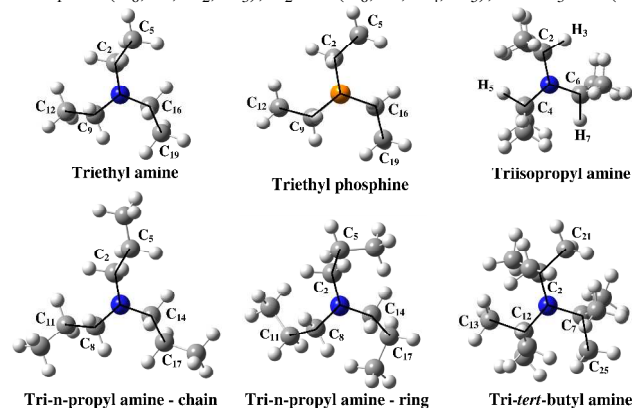
3.2 Related molecules

3.2.1 Triethyl phosphine

Analogous to triethyl amine, three dihedral angles $\alpha_1 = \angle(C_{16}, P, C_2, C_5)$, $\alpha_2 = \angle(C_{16}, P, C_9, C_{12})$, and $\alpha_3 = \angle(C_9, P, C_{16}, C_{19})$ were defined. In this case, 8 starting geometries were calculated, which were based on the structure of the triethyl amine conformers. From these starting geometries, 7 conformers were found. One of them is a saddle point, all others should exist as stable conformers. The most stable conformer of triethyl phosphine (indicated in Figure 5) has the known propeller-like structure and is consequently an oblate top. However, the ethyl groups are not tilted in the direction of the free electron pair, but are located almost in a plane containing the phosphorous atom.

3.2.2 Triisopropyl amine, tri-n-propyl amine, and tri-*tert*-butyl amine

In the case of triisopropyl amine, the H_3, H_5, and H_7 atoms can be considered as the methyl groups C_5, C_{12}, and C_{19} of triethyl amine, respectively. On the other hands, the methyl groups can be seen as the protons. Therefore, the dihedral angles were chosen to be $\alpha_1 = \angle(C_6, N, C_2, H_3)$, $\alpha_2 = \angle(C_6, N, C_4, H_5)$, and $\alpha_3 = \angle(C_4,$

N, C_6, H_7) in order to enable a direct comparison with the conformers of triethyl amine. After optimizations, 8 conformers were found and 7 of them represent true minima. Once again, a propeller-like structure was found for the most stable conformer. In the case of tri-n-propyl amine, many starting geometries are possible due to the long alkyl chains. Therefore, we began only with the starting geometries based on the most stable conformer III of triethyl amine. Two conformers were found, one with a zigzag chain structure, the other with a ring structure. The propeller-like structure is conserved in both cases.

For tri-*tert*-butyl amines, only one conformer could be found, once again with the propeller-like structure, and existing as an enantiomeric pair. For comparison, the most stable conformers of all molecules are shown in Figure 5. It should be noted that all of them are oblate tops. The energy values, dipole moments, and rotational constants of all conformers, as well as the Cartesian coordinates of the most stable conformers are given in the supplementary material in Table S-4.

4. Microwave spectrum

4.1 Main isotopologue

Conformer III of triethyl amine is most stable. Therefore, it is expected to be observed under molecular beam conditions, where the rotational temperature is often very low, approximately 2 K. The rotational energy levels can be calculated using the rotational constants from quantum chemical results. Using the spectrometer described in ref. [6,7], small scans of about 20 MHz around the predicted frequency of the transitions $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ were recorded. Approximately 5 MHz broad multiplets were found due to the hyperfine quadrupole splittings of the ^{14}N nucleus. These frequency ranges were remeasured in the high resolution mode in a grid of 0.25 MHz. A typical spectrum is shown in Figure 6, the complete scan of the $J = 3 \leftarrow 2$ transition in Figure 7. At the beginning, 10 lines of the $J = 2 \leftarrow 1$ and 12 lines of the $J = 3 \leftarrow 2$ transition were found and fitted with the program *spfit/spcat* written by Pickett.[12] A more accurate theoretical spectrum could be predicted with the fitted parameters. Further lines of the transitions $J = 4 \leftarrow 3$ and $J = 5 \leftarrow 4$ could be measured directly in the high resolution mode. In total, 48 lines were found, assigned, and fitted. The fitted molecular parameters are given in Table 2, a list of ten $J = 2 \leftarrow 1$ transitions in Table 3. The complete data set as well as the parameter definition (*.par) file of the program *spfit* can be found in supplementary material (Table S-5 and S-6).

Fig. 5 The propeller-like structure found in triethyl amine and related molecules
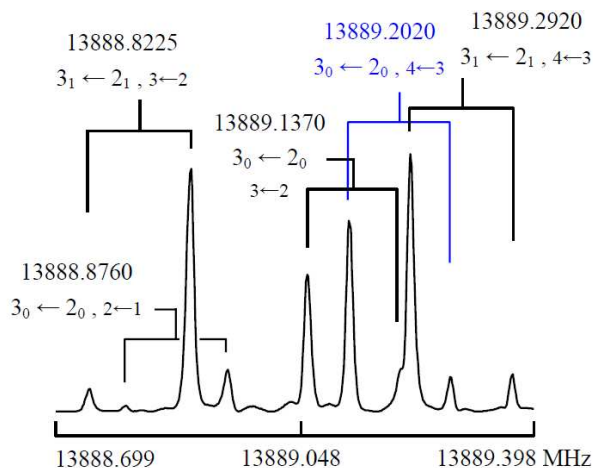
Fig. 6 A typical spectrum of the $3_K \leftarrow 2_K$, $F \leftarrow F$ transition of triethyl amine measured in the high resolution mode. Doppler splittings are marked by brackets. For this spectrum, 601 FID were co-added.

Table 3. Observed frequencies ($\nu_{Obs.}$) of ten $J = 2 \leftarrow 1$ transitions of the main isotopologue of triethyl amine. $\nu_{Calc.}$ is the calculated value; $\nu_{Obs.} - \nu_{Calc.}$ are values obtained after a fit with the program *spfit*. J and K_c are the symmetric top rotational quantum numbers, F is the total angular momentum in the coupled basis with $F = J + I$.

Upper level			Lower level			$\nu_{Obs.}$	$\nu_{Obs.} - \nu_{Calc.}$
J	K_c	F	J	K_c	F	MHz	kHz
2	0	3	1	0	2	9259.5790	1.5
2	0	2	1	0	1	9259.4630	−2.1
2	0	2	1	0	2	9257.8925	0.5
2	0	1	1	0	1	9262.0870	−0.6
2	0	1	1	0	2	9260.5150	0.6
2	1	1	1	1	0	9261.4380	−0.6
2	1	2	1	1	1	9258.1610	0.2
2	1	3	1	1	2	9259.7895	−0.5
2	1	2	1	1	2	9258.9470	−0.2
2	1	1	1	1	2	9260.2590	0.3

4.2 ^{13}C isotopologue

In addition to the rotational spectrum of the main ^{12}C isotopologue, several lines of ^{13}C isotopologues could be observed. With 6 carbon atoms, many ^{13}C isotopologues are available; however, some of them are equivalent. They are the isotopologues with ^{13}C substituent at the C_2, C_9, and C_{16} positions and at the C_5, C_{12}, and C_{19} positions. In both cases, the frequency of occurrence increases from approximately 1.1% to 3.3%. Therefore, it is possible to measure these isotopologues in their natural concentrations.

The Cartesian coordinates of conformer III obtained from the program *Gaussian09* were transformed to principal axes coordinates. The mass of the substituted ^{12}C atom was changed to that of the ^{13}C atom. The rotational constants were calculated and used as starting values to predict the theoretical spectrum with the program *spcat*.[12] All lines were measured directly in the high resolution mode. In total, 16 transitions of the $^{13}C_2$- and 10 transitions of the $^{13}C_5$ isotopologue were assigned and fitted. It should be noted that the molecule becomes asymmetric due to the ^{13}C substituent and is no longer an oblate top. Therefore, the C rotational constants could be determined. All fitted transitions are listed in Table S-7 and S-8 in the supplementary material. The molecular parameters can be found also in Table 2 with the main
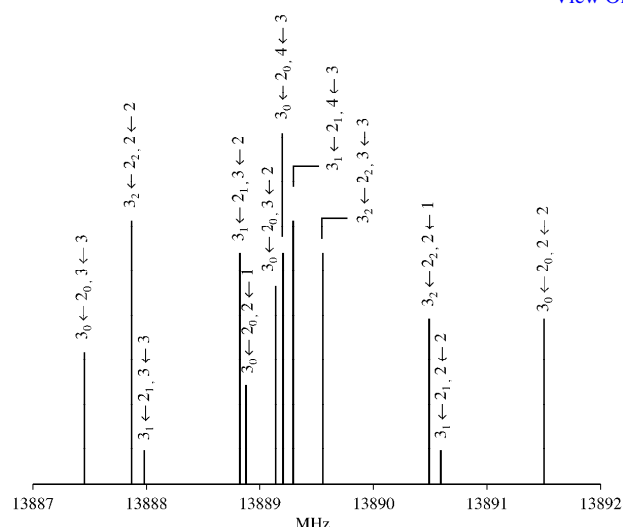
Fig. 7 The complete scan of the $3_K \leftarrow 2_K$, $F \leftarrow F$ transition of triethyl amine measured in the high resolution mode in a grid of 0.25 MHz. The intensity is estimated.

isotopologue. The parameter definition (*.par) files of the program *spfit* are also given in Table S-5.

5. Results and discussion

The structure of triethyl amine obtained by microwave spectroscopy has some interesting aspects. Even though this molecule is relatively large with 22 atoms, its most stable conformer is an oblate top. It has the propeller structure and is thereby chiral. The triethyl amine propeller can have a clockwise or anti-clockwise direction, depending on the respective enantiomer.

The rotational transitions of the main isotopologue are located within several small frequency ranges and could be found easily in the spectrum. All recorded lines were assigned and fitted with a standard deviation of 1.5 kHz, within the experimental accuracy. The A and B rotational constants calculated on the MP2/6-311++G(d,p) level were reasonable starting values. The absolute deviation was only 4 MHz (0.2%). Determination of the C rotational constant is not possible for this oblate top.

Calculations of the quadrupole coupling constants for diethyl amine at the MP2/6-311++G(d,p) level yielded the χ_{aa} value with a deviation of 3.4%. For the $\chi_{bb} - \chi_{cc}$ and the χ_{bc} value, the deviations are considerably larger (11% in both cases).[2] Electric field gradient calculations of Bailey on this molecule[13] at the B3PW91/6-311+G(d,p) level of theory based on the optimized structure at the MP2/6-311+G(df,pd) level using the correction factor eQ/h of 4.5617(43) MHz/a.u.[14] could calculate the coupling constants almost exactly to the experimental values. Therefore, we assumed that optimizations with the MP2 method yield quite reasonable molecular structure parameters. However, for electric field gradient the density functional theory turned out to be much more suitable. A combination of both methods was also used in this case to calculate the quadrupole coupling constant χ_{zz}. The structure was optimized using different methods and basis sets. Afterwards, point calculation of the electric field gradient was carried out with the B3PW91/6-311+G(d,p) level. The results are given in Table 4. Also in this case, the structure optimized at the MP2/6-311+G(df,pd) level of theory yielded the best result which has almost perfect agreement with the experimental value with a deviation of 0.03%.

Table 4. The χ_{zz} quadrupole coupling constant (in MHz) of ^{14}N in triethyl amine. The electric field gradient was calculated at the B3PW91/6-311+G(d,p) level whereas the structure was optimized with a different method and basis set.

Basis set	χ_{zz}
B3PW91/6-311+G(d,p)	−5.4585
MP2/6-311+G(d,p)	−5.2566
MP2/6-311++G(d,p)	−5.3498
MP2/6-311+G(df,pd)	−5.2461
MP2/6-311+G(3df,3pd)	−5.3011

The symmetric top character of triethyl amine allows a direct comparison of the χ_{zz} quadrupole coupling constant with other symmetric top molecules like nitrogen trifluoride, ammonia, trimethyl amine, and quinuclidine (see Table 5). The χ_{zz} value of triethyl amine is determined to be −5.2444 MHz, almost the same as the value of −5.1915 MHz found for quinuclidine.[4] The corresponding value of −5.47 MHz reported for trimethyl amine[3] is slightly higher. It is interesting to compare this value with values for ammonia[1] and nitrogen trifluoride NF$_3$,[5] which are −4.0842 MHz and −7.903 MHz, respectively. The value for ammonia is much lower and the one for nitrogen trifluoride much higher. This effect might be due to the different inductive effects of these substituents. In the case of triethyl amine and quinuclidine, the substituents are carbon chains, whereas only methyl groups exist in trimethyl amine. However, all of these alkyl substituents have a positive inductive effect. In the case of ammonia, the protons have no inductive effect. For nitrogen trifluoride, the negative inductive effect of the fluorine atoms might have influence on the quadrupole constant.

Table 5. The χ_{zz} quadrupole coupling constant (in MHz) of ^{14}N in triethyl amine. The electric field gradient was calculated at the B3PW91/6-311+G(d,p) level whereas the structure was optimized with a different method and basis set.

	χ_{zz}[a]
nitrogen trifluoride[5]	−7.903
ammonia[1]	−4.0842
triethyl amine	−5.2444
quinuclidine[4]	−5.1915
trimethyl amine[3]	−5.47

[a] $\chi_{xx} = \chi_{yy} = -0.5\chi_{zz}$

The rotational transitions of the ^{13}C isotopologues could be fitted with an excellent standard deviation of lower than 0.5 kHz in both cases. The A rotational constant is almost the same as the one of the main isotopologue, however, the B constants are appreciably lower. The difference is 22.1 MHz and 63.6 MHz for the ^{13}C$_2$ and the ^{13}C$_5$ isotopologue, respectively. Unlike the ^{12}C isotopologue, the C rotational constant could be determined and has almost exactly the value calculated at the MP2/6-311++G(d,p) level of theory.

Using Kraitchman's molecular structure determination,[15] the projections of the C$_2$- and C$_5$-atoms on the C$_3$ symmetry axes can be determined. For the C$_2$ atom, $|y| = 1.38774(86)$ Å and $|z| = 0.4269(28)$ Å were found. For the C$_5$ atoms, the respective values are $|y| = 2.45489(49)$ Å and $|z| = 0.4267(28)$ Å. The standard deviation is determined using equation (5.38) in ref.[16]. It should be noted that the $|z|$ values for the C$_2$ and C$_5$ atoms are identical. However, the optimized structure calculated at the MP2/6-311++G(d,p) level has shown that one of the z values is positive and the other one is negative, i.e. the plane through the center of mass and vertical to the C$_3$ axes is exactly in the middle of the C$_2$ and C$_5$ atoms. The determined values are very close to the calculated ones of $(|y|, |z|) = (1.3918$ Å, 0.4269 Å) and

$(2.4557$ Å, 0.4267 Å) for the C$_2$ and C$_5$ atoms, respectively. Unfortunately, the C$_2$–C$_5$ bond length could not be determined since information on the ^{15}N isotopologue is missing. No lines of the ^{15}N isotopologue can be observed because the ^{15}N transitions are located almost at the same position where the strong ^{14}N transitions also exist.

Finally, it should be mentioned that no additional splittings were found in the spectrum. This means that the splittings due to internal rotation of the three methyl groups are very small and cannot be resolved even in the high resolution mode. The reason might be a somewhat higher barrier than that we observed in diethyl amine or a more complex spectrum caused by three internal rotors where many unresolved torsional components overlap resulting in broadened lines.

6. Conclusions

The propeller-like structure of triethyl amine with two possible enantiomers was found by a combination of microwave spectroscopy and quantum chemistry. The rotational constants could be determined within the experimental accuracy of 1.5 kHz using the program *spfit/spcat* written by Pickett. The structure was confirmed by the results obtained from two isotopologues measured in their nature abundances using Kraitchman's equation. Theoretical calculations on the transition state and some related molecules were carried out. Furthermore, the χ_{zz} quadrupole coupling constant could be calculated exactly to the experimental value using Bailey's method reported in ref.[14]. A direct comparison with some other symmetric top molecules supports that the inductive effect might influent this parameter.

Acknowledgements

Notes and references

[a] *Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52074 Aachen, Germany. Fax: +49 241 80 92365; Tel: +49 241 80 94759; E-mail: nguyen@pc.rwth-aachen.de*

† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/
1   G. R. Gunther-Mohr, R. L. White, A. L. Schawlow, W. E. Good, D. K. Coles, *Phys. Rev.*, 1954, **94**, 1184.
2   H. V. L. Nguyen, W. Stahl, *J. Chem. Phys.*, 2011, **135**, 024310.
3   J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, 1969, **51**, 1580.
4   D. Consalvo and W. Stahl, *J. Mol. Struct.*, 1998, **447**, 119.
5   S. E. Novick, W. Chen, M. R. Munrow, K. J. Grant, *J. Mol. Spectrosc.*, 1996, **179**, 219.
6   U. Andresen, H. Dreizler, J.-U. Grabow, W. Stahl, *Rev. Sci. Instrum.*, 1990, **61**, 3694.
7   J.-U. Grabow, W. Stahl, H. Dreizler, *Rev. Sci. Instrum.*, 1996, **67**, 4072.
8   Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E.

Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

9   D. Jelisavac, D. Cortés-Gómez, H. V. L. Nguyen, L. W. Sutikdja, W. Stahl, and I. Kleiner, *J. Mol. Spectrosc.*, 2009, **257**, 111.

10   H. V. L. Nguyen and W. Stahl, *J. Mol. Spectrosc.*, 2010, **264**, 120.

11   H. Mouhib, Y. Zhao, W. Stahl, *J. Mol. Spectrosc.*, 2010, **261**, 59.

12   H. M. Pickett, *J. Mol. Spectrosc.*, 1991, **148**, 371.

13   http://web.mac.com/wcbailey/nqcc/Diethylamine.html

14   W. C. Bailey, *Chem. Phys.*, 2000, **252**, 57.

15   J. Kraitchman, *Amer. J. Phys.*, 1953, **21**, 17.

16   J. Demaison, J. E. Boggs, A. G. Császár, Equilibrium Molecular Structures: From Spectroscopy to Quantum Chemistry, CRC Press, Boca Raton, FL, 2011.

Table of contents entry

Color graphic:
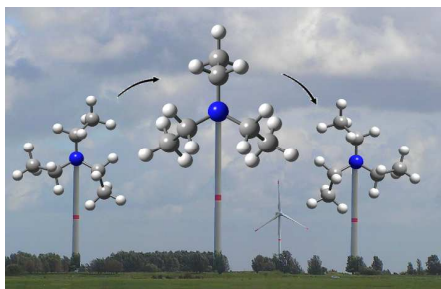
Text:

The energetically favorable structure of triethyl amine has a chiral propeller form with a C_{3v} symmetry transition state.