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Three Intermolecular Bonds Form a Weak but Rigid Complex: $O(CH_3)_2\cdots N_2O$

Kenji Yamanou, Yoshio Tatamitani, and Teruhiko Ogata*

Department of Chemistry, Faculty of Science, Shizuoka University 836 Ohya, Suruga-ku, Shizuoka, Japan 422-8529

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The rotational spectrum of the dimethylether (DME)-N_2O complex has been studied for the normal and three ^{15}N isotopomers, leading to rotational, centrifugal distortion, and nuclear quadrupole coupling constants, the molecular structure, and a binding energy of 8.4 kJ mol^{-1}. Here, it is shown that many DME-N_2O-type complexes are bound with three intermolecular bonds and that the internal rotation splitting due to the methyl groups in the rotational spectrum was fixed by complexation, implying that many weak intermolecular bonds can fix the flexible motions and maintain a rigid structure. If the model we are proposing for DME-N_2O-type complexes can be applied to biomolecules, it may give something a clue to solve the biological riddle on the dynamic character of biomolecules that have conflicting properties of being rigid and binding weakly.

Introduction

Over the past quarter century, a large number of van der Waals complexes have been studied by high resolution molecular spectroscopy.[1] An interesting type of complex among those is the triply bonded van der Waals complex. A dimethylether (DME) dimer, for example, is bounded by three hydrogen bonds between two methyl hydrogens and a counterpart oxygen and between oxygen and one counterpart methyl hydrogen, which fix the internal rotations of three of the methyl groups to four and allows it to behave like a one-top molecule.[2] In the living world, although static structures are known for many proteins, the functions of proteins are governed ultimately by their dynamic character.[3] For proteins, therefore, the lower binding energy is preferable for frequent associations and dissociations; whereas a biomolecule must maintain its definite structure with these weak inter/intramolecular bonds. It is one of the riddle of the dynamic character of biomolecules. These apparently conflicting conditions in the living world, however, can be accomplished by a simple simpler complex with many torsion motions and weak intermolecular hydrogen bonds as below.

van der Waals complexes of dimethylether exhibit a rather versatile rotational spectrum depending on the barrier height to internal rotation of the methyl groups. Complexes of DME with the linear triatomic molecules OCS, CO_2, and CS_2 have been studied by Peebles et al.[4] and exhibit a wide variation in their rotational spectra and structures. The DME-OCS and DME-CO_2 complexes possess a structure in which the linear triatomic molecule is located in the heavy atom plane of DME, aligned approximately perpendicular to its C_2 axis, while that of the DME-CS_2 complex is T-shaped with the CS_2 lying approximately along the lone pair direction of the DME oxygen, and the CS_2 tunnels between the lone pairs of DME. The complexes exhibit no internal rotation spectrum splitting, meaning that the internal rotation of the methyl groups in the DME monomer[5] (Figures 1a) is frozen by the complexation (parts b−d of Figure 1). The rotational spectrum of DME-N_2O, isoelectronic to these complexes, is expected to give interesting comparisons and is the logical extension to this series, particularly in light of the methyl internal rotation splitting, which depends on the complexation.

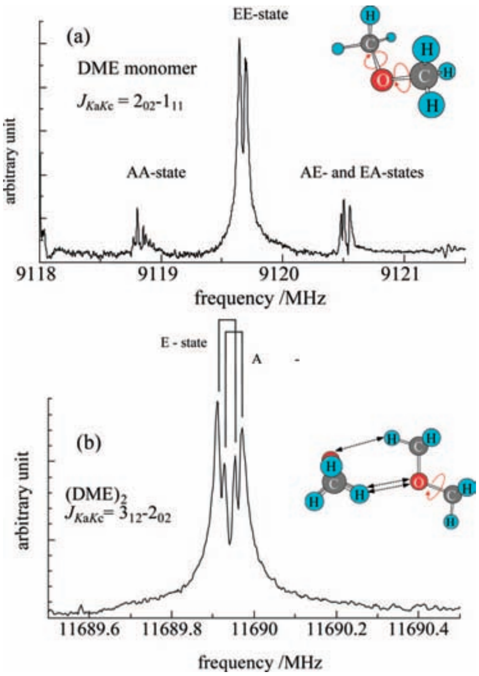

Figure 1. FTMW spectra of the DME monomer, DME dimer, and DME-N_2O complexes. (a) The spectrum of the DME monomer splits into four states due to the internal rotation of two methyl groups, and each state exhibits a Doppler doublet. (b) The spectrum of the DME dimer splits into two states due to the internal rotation of one free methyl group, and each state exhibits a Doppler doublet. The three other methyl groups were fixed by the complexation. (c) The spectrum of normal DME-N_2O complex splits into multiplet components due to two ^{14}N nuclear quadrupole couplings, and each components exhibits a Doppler doublet but no internal rotation splitting. (d) The spectrum of DME-$^{15}N_2O$ DME exhibits a singlet spectrum with a Doppler doublet but no internal rotation splitting.

It is interesting in relation to a biomolecule to see if the internal rotation of the methyl groups can be fixed by weak intermolecular bonds. We therefore studied the FTMW spectrum of the DME-N_2O complex and made comparisons with those of other related complexes.

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* To whom correspondence should be addressed.. E-mail: sctogat@ipc.shizuoka.ac.jp (T.O.). Phone: +81-54-237-3477. Fax: +81-54-237-3477.

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TABLE 1: Observed and Calculated Spectroscopic Constants of Normal DME-N$_2$O

	DME-N$_2$O		
parameter	experiment 1	experiment 2	ab initio[b]
A/MHz	5601.915(12)	5605.002(31)	5633.3107
B/MHz	1896.04475(43)	1896.00618(17)	1916.1204
C/MHz	1442.69656(41)	1442.72903(19)	1456.3898
Δ_J/kHz	2.7499(29)	2.859(17)	
Δ_{JK}/kHz	7.258(16)	0.914(46)	
Δ_K/kHz	−122.2(56)	−385(15)	
δ_J/kHz	0.6798(14)		
δ_K/kHz	5.61(21)		
χ_{aa} (N$_t$[c])/MHz	0.36359(61)	0.38478(66)	
χ_{bb}(N$_t$) − χ_{cc}(N$_t$)/MHz	−1.1535(30)	−1.1720(39)	
χ_{aa}(N$_c$[d])/MHz	0.05099(60)	0.13013(66)	
χ_{bb}(N$_c$) − χ_{cc}(N$_c$)/MHz	−0.3284(26)	−0.5050(38)	
P_{cc}[e]/u Å^2	−3.229	−3.211	−3.179
N[f]	126	48	

Bond Axes System

parameter	experiment 1	experiment 2	N$_2$O monomer [g]
χ_{xx}(N$_t$)/MHz	0.3636	0.3385	0.38688(14)
χ_{yy}(N$_t$)/MHz	0.3949	0.3936	0.38688(14)
χ_{zz}(N$_t$)/MHz	−0.7588	−0.7785	−0.77376(27)
χ_{xx}(N$_c$)/MHz	0.0510	0.1302	0.13379(19)
χ_{yy}(N$_c$)/MHz	0.1387	0.1874	0.13379(19)
χ_{zz}(N$_c$)/MHz	−0.1897	−0.3176	−0.26758(38)

[a] Numbers in parentheses denote one standard deviation of the least-squares fitting in units of the last significant digits. [b] CCSD/6-211++(d,p) level. [c] Terminal nitrogen. [d] Central nitrogen. [e] Second moments of inertia. [f] Number of fitted transitions; [g] Reference 5.

Experimental Methods

A sample of N$_2$O was purchased from Takachiho Chemical Industrial Co., Ltd., and used without further purification. The sample of the ^{15}N substituted isotopomers were prepared from 10 at % ammoniumnitrate $^{15}\mathrm{NH}_4{}^{15}\mathrm{NO}_2$ purchased from ISOTEC, Inc. by heating up to 140 °C. The DME-N$_2$O complexes were generated by supersonic expansion at conditions optimized for 1:1 cluster formation, 1% DME and 1% N$_2$O in 98% Ar or in 98% Ne.

The FTMW spectrum was measured using a pulsed-beam Fabry−Perot cavity Fourier-transform microwave spectrometer of the Balle-Flygare type[6] at Shizuoka University.[2] For this instrument, the frequency range is 4−19 GHz. The frequency standard is a synthesizer HP 83650 L, and accuracy in the frequency measurements is estimated to be 0.5 kHz. The vacuum chamber is a stainless steel cylinder 45 cm in diameter and 80 cm in length. The chamber is evacuated with a 14-in. diffusion pump and a 600 m^3/h mechanical booster pump. The diameter of the aluminum mirrors is 26 cm, and they are separated by 40 cm. The gas mixture was passed through the solenoid valve (General Valve, Series 9 with the nozzle diameter of 0.8 mm) at a backing pressure of $\sim$2 bar and expanded into the cavity. The frequencies were determined after Fourier transformation of the 8000 data point time domain signal, recorded in 100-ns sample intervals. The pulsed-nozzle valve is mounted near the center of one of the mirrors in such a way that the supersonic beam propagates parallel to the resonator axis. Because of this setup, all lines appear as Doppler doublets. The line position is the arithmetic mean of both Doppler components.

Ab initio MO calculations of the DME-N$_2$O complexes were performed to evaluate structure, dissociation energy, and electric dipole moments. Various methods and basis sets within Gaussian 03 software package were examined.[7] The MP2/6-211++G** and CCSD/6-211++G(d,p) levels of calculation were generally employed, because they reproduced the experiments well. The calculated structures and dissociation energy have been compared with those experimentally derived.

Results and Discussions

For the assignments of the observed spectrum and analysis, the preliminary rotational constants of DME-N$_2$O were estimated

TABLE 2: Spectroscopic Constants of the ^{15}N-Substituted DME-N$_2$O Complexes

parameters	DME-N^{15}NO	DME-^{15}NNO	DME-^{15}N^{15}NO
A/MHz	5601.518(16)	5514.993(13)	5515.176(29)
B/MHz	1875.88249(59)	1875.39936(42)	1856.10175(99)
C/MHz	1430.96818(56)	1424.97960(39)	1413.78885(96)
Δ_J/kHz	2.6919(32)	2.6065(34)	2.6137(34)
Δ_{JK}/kHz	7.214(15)	7.234(17)	7.029(18)
Δ_K/kHz	−154 (8)	−167.5(64)	−68 (15)
δ_J/kHz	0.6838(18)	0.6440(22)	0.6504(29)
δ_K/kHz	4.39(28)	2.67(19)	6.27(50)
χ_{aa}(N_t[b])/MHz	0.33139(55)		
χ_{bb}(N_t) − χ_{cc}(N_t)/MHz	−1.0668(24)		
χ_{aa}(N$_c$[c])/MHz		0.06779(52)	
χ_{bb}(N$_c$) − χ_{cc}(N$_c$)/MHz		−0.4080(96)	
P_{cc}[d]/uÅ^2	−3.229	−3.230	−3.225
N[e]	77	88	20

Bond Axes System

parameters	DME-N^{15}NO	DME-^{15}NNO	DME-^{15}N^{15}NO
χ_{xx}(N$_t$)/MHz	0.3314		
χ_{yy}(N$_t$)/MHz	0.3677		
χ_{zz}(N$_t$)/MHz	−0.6991		
χ_{xx}(N$_c$)/MHz		0.0684	
χ_{yy}(N$_c$)/MHz		0.1701	
χ_{zz}(N$_c$)/MHz		−0.2385	

[a] Numbers in parentheses denote one standard deviation of the least-squares fitting in units of the last significant digits. [b] Terminal nitrogen. [c] Central nitrogen. [d] Second moments of inertia. [e] Number of fitted transitions.

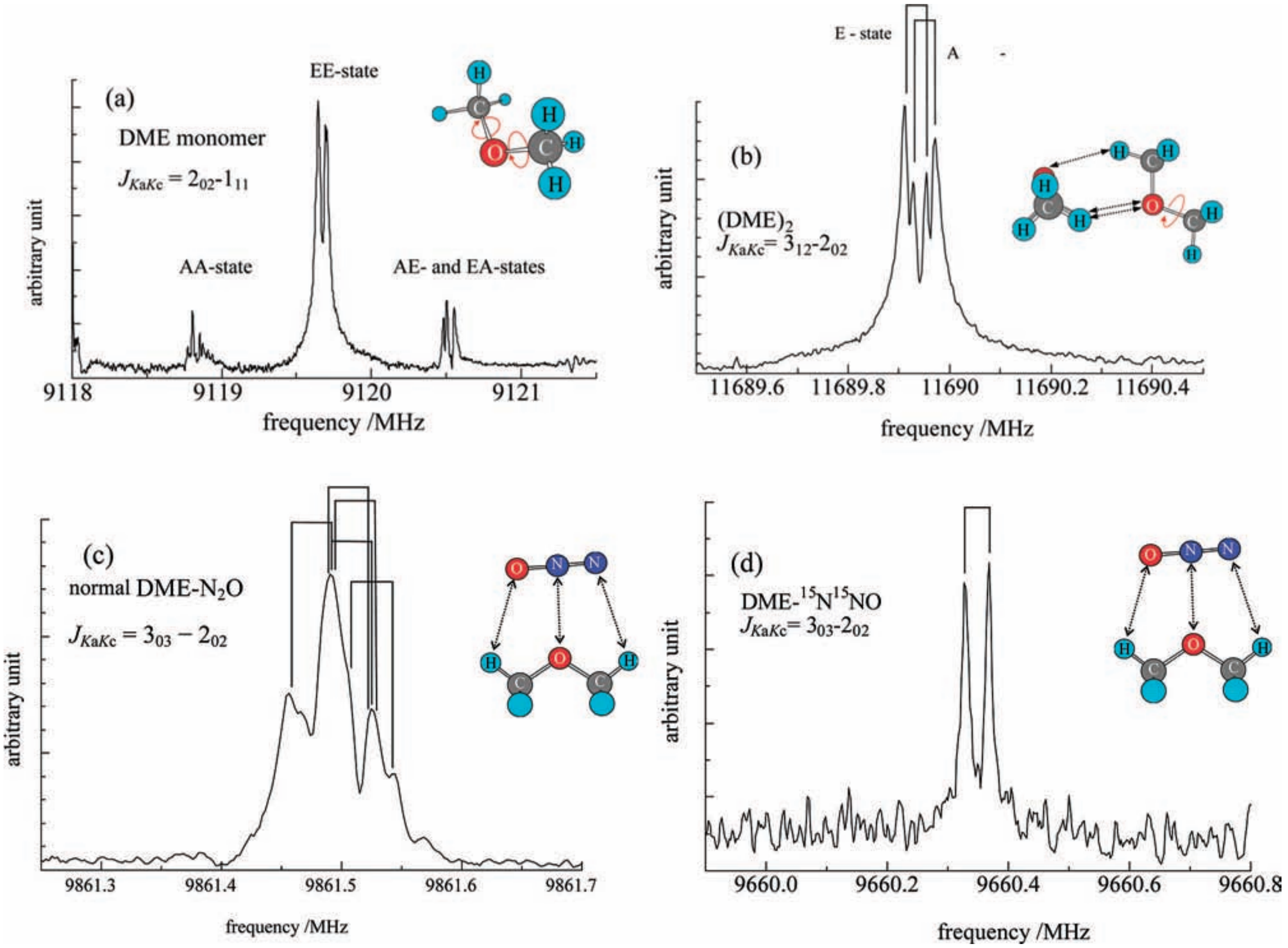

Figure 2. Structure of the DME···N$_2$O complex.

using the molecular structure based on an ab initio calculation in which four possible conformers were identified, including two parallel-types and two linear types by the Gaussian MP2/6-211++G(2d,2p) level of calculation. The lowest energy complex is one of the parallel-type structures: all heavy atoms in the complex are coplanar, and the line joining the H, O, H atoms in DME is approximately parallel to the axis of the N$_2$O. The observed spectrum pattern resembled that calculated by this conformer. Only a-type rotational transitions were observed, suggesting a smaller b-dipole moment component. The calculated b-dipole moment of 0.39 D is too small to account for the observation of b-type transitions, because the spectrum is split into many hyperfine components due to the two nitrogen-14 nuclei. Attempts to locate c-type transitions at their predicted frequencies were not successful, although an absence of a c-type line is consistent with the plane of symmetry resulting from analysis of the structural data and ab initio calculated values of the dipole moments $\mu_a = 1.80$ D, $\mu_b = 0.39$ D, and $\mu_c = 0.00$ D.

The rotational spectrum of the DME-N$_2$O complex exhibits complicated splittings due to the nuclear quadrupole couplings of the nitrogen-14 nuclei of the central and terminal N atoms, as does the singlet spectrum for the ^{15}N^{15}NO species (parts c and d of Figure 1). The 140 and 70 measured components transitions for normal and ^{15}N isotopomers, respectively, are listed in Tables 1 and 2 of Supporting Information, along with the residuals from a least-squares fit of the transition frequencies to a Watson A reduction Hamiltonian in the I^r representation[8] (using the SPFIT program of Herb Pickett[9]). The spectroscopic constants determined are shown in Table 1. Since all split lines were assigned to the hyperfine components, no obvious indication of internal rotation splittings were observed (Figure 1c). The lack of observed splittings in the current work indicates that the barrier to internal rotation in this complex is changed relative to the DME monomer,[5] the spectrum of which contains splittings of the order of a few megahertz (Figure 1a). As shown in Tables 1 and 2, the numerical values of the nuclear quadrupole coupling constants of the central nitrogen atom are smaller than those of the terminal one are because of the more centrosymmetric electronic distribution around the central nitrogen atom. This means that the numerical values of the parameters to be fitted with the least-squares fit were small, leading to relatively large errors. Thus, the values of the quadrupole coupling constants for the central nitrogen are more sensitive to the fit than those for the terminal ones are. This can be seen for the least-squares fit of the data from experiment 1 and experiment 2 in Table 1, where the values for experiment 2 were closer to the corresponding values for the N$_2$O monomer. In the same way, the quadrupole coupling constants for the central nitrogen atom in the DME-^{15}N^{14}NO complex deviate from those of the N$_2$O monomer in Table 1. Thus, the values for the central nitrogen atoms generally depend on the fit; however, these uncertainties were not included in the errors quoted in Tables 1 and 2. The structure of DME-N$_2$O shows three hydrogen bonds between the H, O, and H atoms in DME and the N, N, and O atoms in N$_2$O, respectively. Similar to that of DME-N$_2$O, the rotational spectra for DME-OCS and DME-CO$_2$ exhibit a singlet spectrum with a triple hydrogen bond (Figure 1 of Supporting Information).

TABLE 3: Structural Parameters of the DME-N_2O Complex

	this work	ab initio
$R_{N\cdots O}$/Å	2.813	2.766
θ_1/deg	88.2	87.6
θ_2/deg	125.8	125.0
R_{cm}/Å	3.354	3.315

TABLE 4: Force Constants and Binding Energies of the DME-N_2O and Related Complexes[13–19]

complex	k_s/Nm^{-1}	E_B/kJ mol^{-1}	reference
DME···Ne	1.0	1.0	13
DME···Ar	2.3	2.5	14
DME···Kr	2.6	2.9	15
DME···Xe	3.0	3.7	16
DME···DFE	3.55	4.76	17
DME···TFE	4.45	5.98	17
DME dimer	4.7	5.7	2
DME···OCS	6.7(2)	7.1(2)	4a, 4b
DME···CO_2	10.9(2)	9.7(2)	4b
DME···CS_2	2.57(6)	5.0(2)	4c
DME···N_2O	8.9	8.4	This work.
DME···HF	12(2)	9(2)	19

The structure of the DME-N_2O complex is determined from the observed rotational constants for the normal and the ^{15}NNO, N^{15}NO, and ^{15}N^{15}NO isotopomers (Tables 1 and 2). Further corroboration of this proposed structure was available from an inspection of second-moment data for the various isotopomers of the complex. The second moment, P_{cc}, depends on the c-principal-axis coordinates of the atoms according to

$$P_{cc} = \sum_i m_i c_i^2 \qquad (1)$$

where m_i is the mass of atom i and c_i is the c coordinate of the atom. In the case of a heavy-atom planar arrangement for this dimer, we would expect the P_{cc} values for all isotopomers to be similar to each other as well as close in magnitude to the P_{cc} value of the DME monomer 3.207 uÅ^2.[10] The P_{cc} of all species in Tables 1 and 2 is close to that of the DME monomer, implying that the heavy atoms in the DME-N_2O are coplanar. The small difference between the monomer and dimer values is due to vibrational contamination from low-frequency van der Waals modes within the complex. Twelve observed moments of inertia enabled a fit to the three structural parameters that are required to describe the dimer geometry (the $N_c\cdots O_D$ distance, the $O_D\cdots N_c{-}O_N$ angle, θ_1, and the $N_c\cdots O_D{-}C_t$ angle, θ_2); see Figure 2 for atom numbering. The geometries of both the DME[10] and N_2O[11] monomers were fixed at their literature values during the fitting process. The parameters derived from the inertial fit are shown in Table 3, along with an estimation of the best value.

The $H\cdots O_N$ and $H\cdots N_t$ distances derived from the fitted structure are 2.95 and 3.15 Å, respectively. It is interesting to note that these distances are longer than the sum of the van der Waals radii of the H, O, and N atoms (H = 1.20, O = 1.52, N = 1.55 Å).[12] The intermolecular $N_c\cdots O_D$ bond length in the DME-N_2O complex is found experimentally to be 2.813 Å and is similar to the ab initio estimate of 2.766 Å.

The force constants and dissociation energies derived from the centrifugal distortion constants are shown in Table 4 and are compared with those for dimers containing DME. The basis set superposition errors in the ab initio calculations and the zero-point energies have not been considered due to the computing time. For DME-N_2O, the dissociation energy is calculated to be 8.4 kJ/mol, meaning that less than 3 kJ/mol is enough for the reduction of each internal rotation. The rotational spectra of the triply bound van der Waals complexes are shown in Figures 1 and S1 of Supportin Information. The internal rotation splittings with a free DME monomer are generally reduced by the complexation. A triple intermolecular bond forms a weak but rigid complex. It is presumably the same as that in biomolecules such as DNA or proteins, where most flexible motions caused by the single bond torsions are efficiently fixed with a small amount of binding energy but many bonds and maintain a definite structure.

Conclusions

1. The rotational spectrum of the DME-N_2O complex has been studied for the normal and three ^{15}N isotopomers, leading to the rotational, centrifugal distortion, and nuclear quadrupole coupling constants of ^{14}N, the molecular structure, and determination of the binding energy to be 8.4 kJ mol^{-1}. The structure of DME-N_2O has N_2O located in the heavy atom plane of the DME and aligned approximately perpendicular to its C_2 axis, with the O atom of N_2O tilted toward the DME.

2. Here we showed many DME-N_2O-type complexes bound with three intermolecular bonds, and the internal rotation splitting due to the methyl groups in the rotational spectrum was fixed by complexation, implying that many weak intermolecular bonds can fix flexible motions and maintain a rigid structure.

3. In living tissue, biomolecules prefer a lower intermolecular binding energy for frequent dissociations and associations; however, they must maintain a definite structure with these weak intermolecular bonds. This work may give something a clue to solve the biological riddle on the dynamic character of biomolecules.

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Supporting Information Available: Experimental details, observed transition frequencies, and rotational spectra of DME complexes. This material is available free of charge via the Internet at http://pubs.acs.org

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