

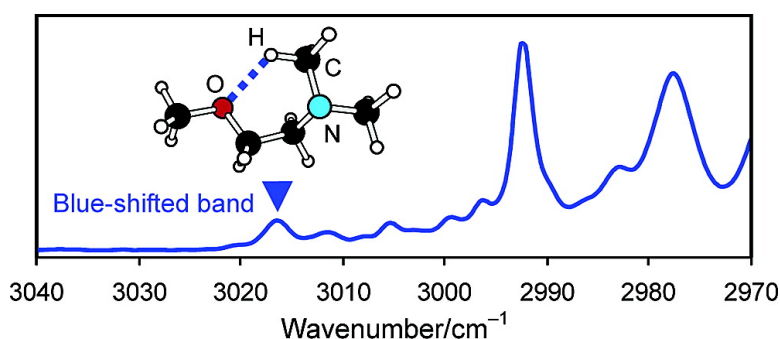
Communication

Experimental Evidence for Intramolecular Blue-Shifting C–H...O Hydrogen Bonding by Matrix-Isolation Infrared Spectroscopy

Hiroatsu Matsuura, Hiroshi Yoshida, Munenori Hieda, Shin-ya Yamanaka, Takanori Harada, Kei Shin-ya, and Keiichi Ohno

J. Am. Chem. Soc., **2003**, 125 (46), 13910-13911 • DOI: 10.1021/ja030538f • Publication Date (Web): 24 October 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 16 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Experimental Evidence for Intramolecular Blue-Shifting C–H···O Hydrogen Bonding by Matrix-Isolation Infrared Spectroscopy

Hiroatsu Matsuura,* Hiroshi Yoshida, Munenori Hieda, Shin-ya Yamanaka, Takanori Harada, Kei Shin-ya, and Keiichi Ohno

Department of Chemistry, Graduate School of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526, Japan

Received September 15, 2003; E-mail: matsuura@sci.hiroshima-u.ac.jp

Recently, C–H···O hydrogen bonding has attracted attention of a large number of researchers in chemistry and biochemistry because of its potential capacity for stabilizing particular structures of molecules and molecular assemblies.^{1–3} C–H···O hydrogen bonds have in fact been recognized as important determinants of the stability and specificity of biological systems.^{4–7} Although this type of hydrogen bonding was found in organic crystals more than 40 years ago,⁸ it was only in the last half of the 1990s when this interaction was accepted widespread as a result, in particular, of theoretical efforts. An intramolecular C–H···O interaction was first suggested for 1,2-dimethoxyethane in the gas phase⁹ and was later confirmed by matrix-isolation infrared spectroscopy.¹⁰ A theoretical study of this molecule has demonstrated the importance of this interaction in the conformational stabilization,¹¹ consistent with the experimental observations.^{9,10,12} Quantum chemical calculations have shown that the formation of the C–H···O hydrogen bond shortens the C–H bond in some molecular systems.^{13–16} The contraction of the C–H bond leads to a blue-shift of the stretching vibrational frequency (wavenumber) of this bond. The unusual blue-shifting hydrogen bonding has received much attention from theoreticians who proposed a number of explanations for this peculiar phenomenon.^{2,3,17–22} The infrared and Raman spectroscopic observations of blue-shifting C–H···O hydrogen bond have been reported in late years.^{23–27} It is noted that the published experimental observations were all for intermolecular C–H···O hydrogen bonds, for example, between the C–H bond of fluoroform and the oxygen atom of dimethyl ether.²⁵ To our knowledge, no experimental evidence has been reported of intramolecular blue-shifting C–H···O hydrogen bonding that determines molecular conformation, although this interaction has been shown to be an important factor of conformational stabilization.^{10,12,13,16,28,29} Our previous study on 1-methoxy-2-(methylthio)ethane predicted a blue-shift of 25 cm⁻¹ for the C–H stretching vibration of the *trans-gauche-gauche'* conformer, but infrared observation of the blue-shifted band was not successful because of its inherent weak intensity.¹⁶ In this work, we have succeeded in observing a blue-shifted infrared band for the TG(T|G') conformer³⁰ of 1-methoxy-2-(dimethylamino)ethane (MDAE) isolated in an argon matrix.

MDAE was prepared by reacting 1-chloro-2-(dimethylamino)ethane with sodium methoxide. Matrix-isolation infrared spectra of MDAE were measured by spraying a premixed gas of argon/MDAE = 1000 onto a cesium iodide plate cooled to 12 K.¹⁶ The effect of annealing was examined by warming the deposited sample to several set temperatures up to 41 K. Energies, structural parameters, and vibrational wavenumbers for 14 possible conformers of MDAE were calculated at the B3LYP/6-311+G** level of density functional theory using the Gaussian 98 program.³¹ The calculations showed that the most stable conformer of MDAE is TG(T|G'), as depicted in Figure 1, and the second most stable is

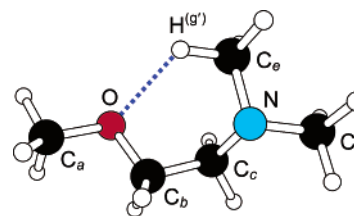


Figure 1. Optimized structure (B3LYP/6-311+G** level) of the TG(T|G') conformer of MDAE. C–H···O hydrogen bonding is indicated by a dotted line.

TT(G|T) with its energy higher than TG(T|G') by 0.54 kJ mol⁻¹. Other conformers are less stable than these two by more than 4 kJ mol⁻¹. The most stable conformer TG(T|G') can form an intramolecular (N)C–H···O hydrogen bond, while TT(G|T) cannot. The high stability of the former is explained by the formation of this hydrogen bond. An examination of the infrared spectra of MDAE in an argon matrix in the 700–1400 cm⁻¹ region revealed that the observed spectra consist of the bands arising from two conformers.³² To identify them, the observed spectra were critically compared with the theoretically calculated spectra of all possible conformers. The comparison shows that the observed bands coincide exclusively with the wavenumbers for TG(T|G') and TT(G|T). The existence of these conformers in an argon matrix agrees with the expectation from the calculated energies. When the sample was annealed at 37 K, the bands of TT(G|T) decreased in intensity relative to the bands of TG(T|G'). As the annealing process induces a transformation of less stable conformers trapped in a matrix into the most stable conformer, TG(T|G') is the most stable in an argon matrix, in agreement with the theoretical prediction.

Having identified the conformers of MDAE present in the matrix, we now examine the matrix-isolation infrared spectra in the C–H stretching region. The observed spectra of the sample before and after annealing and the calculated spectra of TG(T|G') and TT(G|T) are shown in Figure 2. On annealing, bands A, D, and E persist, while bands B and C disappear substantially from the spectra. In consideration of the spectral behavior in the lower-wavenumber region, the former three bands are assigned to the most stable conformer TG(T|G'), and the latter two are assigned to the second most stable conformer TT(G|T). A comparison of the observed spectra with the calculated spectra (Figure 2) ensures these assignments. The calculations indicate that band D is actually assigned to both TG(T|G') and TT(G|T). Several weaker bands observed in this region are convincingly assigned to combination tones and overtones of vibrations.

The wavenumber 3016.5 cm⁻¹ of band E is unusually higher than the wavenumbers of C–H stretching vibrations for this type of molecules. An examination of the calculated results for all conformers of MDAE shows that the wavenumbers of C–H stretching vibrations higher than 3000 cm⁻¹ are found only for TG-

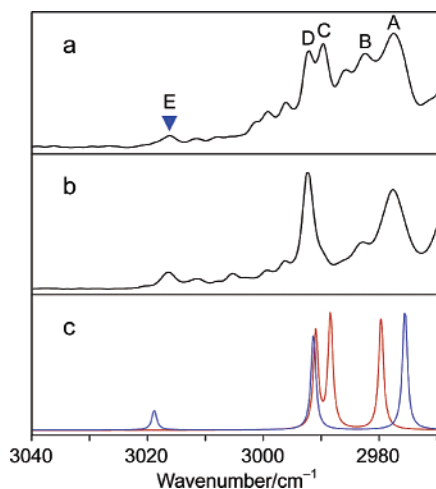


Figure 2. Observed and calculated infrared spectra of MDAE in the 2970–3040 cm^{-1} region: (a) matrix-isolation spectrum at 12 K before annealing, (b) matrix-isolation spectrum after annealing at 37 K, and (c) calculated spectra of TG(T|G') (blue) and TT(G|T) (red). In the observed spectrum a, the blue-shifted C–H stretching band is marked with a blue arrow. The calculated wavenumbers have been scaled by a factor of 0.962.

(T|G') and GG(T|G'), both of which involve C–H \cdots O hydrogen bonding as evidenced by their (C)H \cdots O distances, 2.38 and 2.41 Å, being shorter than the corresponding van der Waals separation by 0.3 Å. The GG(T|G') conformer is much less stable because of the unfavorable gauche conformation around the $C_aO-C_bC_c$ bond. According to the calculated results, band E for TG(T|G') arises from the stretching vibration of the $C_e-H^{(g)}$ bond³³ which participates in the formation of the C–H \cdots O hydrogen bond. To confirm the shortening of this bond, we have examined the C–H bond lengths of the (N)CH₃ groups for TG(T|G') as well as for TG(G|T). The latter is a reference conformer to the former in that its molecular conformation is identical to that of the former except for the opposite direction of the gauche rotation around one of the $C_bC_c-NCH_3$ bonds, giving rise in consequence to no formation of the C–H \cdots O hydrogen bond. The length of the $C_e-H^{(g)}$ bond for TG(T|G') is 1.087 Å, which is 0.004 Å shorter than the corresponding bond length for the reference conformer.³² A comparison of the C–H stretching wavenumbers of the (N)CH₃ groups for the two conformers indicates that the wavenumber of the $C_e-H^{(g)}$ bond for TG(T|G') is blue-shifted by at least 35 cm^{-1} due to C–H \cdots O hydrogen bonding. It may also be important to note the lengthening (0.006 Å) of the N–C bond next to the shortened C–H bond. The present infrared spectroscopic experiments, in combination with density functional calculations, have evidenced a blue-shifted C–H stretching band at 3016.5 cm^{-1} for MDAE. As far as the authors are aware, this is the first experimental observation of intramolecular blue-shifting hydrogen bonding.

Acknowledgment. We thank Prof. Yoosuke Yamamoto of Hiroshima University for his help in the synthesis of MDAE. This work was partially supported by a Grant-in-Aid for Scientific Research No. 10640522 from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Supporting Information Available: Tables of energies of conformers, C–H stretching wavenumbers higher than 2970 cm^{-1} , and

lengths and stretching wavenumbers of the (N)C–H bonds. Infrared spectra in the 700–1400 cm^{-1} region (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: New York, 1999; pp 29–121.
- (2) Scheiner, S. In *Advances in Molecular Structure Research*; Hargittai, M., Hargittai, I., Eds.; JAI Press: Stamford, CT, 2000; Vol. 6, pp 159–207.
- (3) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253–4264.
- (4) Musah, R. A.; Jensen, G. M.; Rosenfeld, R. J.; McRee, D. E.; Goodin, D. B. *J. Am. Chem. Soc.* **1997**, *119*, 9083–9084.
- (5) Wahl, M. C.; Sundaralingam, M. *Trends Biochem. Sci.* **1997**, *22*, 97–102.
- (6) Mandel-Gutfreund, Y.; Margalit, H.; Jernigan, R. L.; Zhurkin, V. B. *J. Mol. Biol.* **1998**, *277*, 1129–1140.
- (7) Senes, A.; Ubarretxena-Belandia, I.; Engelman, D. M. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 9056–9061.
- (8) (a) Sutor, D. *J. Nature* **1962**, *195*, 68–69. (b) Sutor, D. *J. Chem. Soc.* **1963**, 1105–1110.
- (9) Astrup, E. E. *Acta Chem. Scand., Ser. A* **1979**, *33*, 655–664.
- (10) Yoshida, H.; Kaneko, I.; Matsuura, H.; Ogawa, Y.; Tasumi, M. *Chem. Phys. Lett.* **1992**, *196*, 601–606.
- (11) Tsuzuki, S.; Uchimaru, T.; Tanabe, K.; Hirano, T. *J. Phys. Chem.* **1993**, *97*, 1346–1350.
- (12) Yoshida, H.; Tanaka, T.; Matsuura, H. *Chem. Lett.* **1996**, 637–638.
- (13) Yoshida, H.; Harada, T.; Murase, T.; Ohno, K.; Matsuura, H. *J. Phys. Chem. A* **1997**, *101*, 1731–1737.
- (14) Karger, N.; Amorim da Costa, A. M.; Ribeiro-Claro, P. J. A. *J. Phys. Chem. A* **1999**, *103*, 8672–8677.
- (15) Hobza, P.; Havlas, Z. *Chem. Phys. Lett.* **1999**, *303*, 447–452.
- (16) Harada, T.; Yoshida, H.; Ohno, K.; Matsuura, H. *Chem. Phys. Lett.* **2002**, *362*, 453–460.
- (17) (a) Gu, Y.; Kar, T.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411–9422. (b) Scheiner, S.; Kar, T. *J. Phys. Chem. A* **2002**, *106*, 1784–1789.
- (18) Masunov, A.; Dannenberg, J. J.; Contreras, R. H. *J. Phys. Chem. A* **2001**, *105*, 4737–4740.
- (19) Li, X.; Liu, L.; Schlegel, H. B. *J. Am. Chem. Soc.* **2002**, *124*, 9639–9647.
- (20) Hermansson, K. *J. Phys. Chem. A* **2002**, *106*, 4695–4702.
- (21) Qian, W.; Krimm, S. *J. Phys. Chem. A* **2002**, *106*, 6628–6636.
- (22) Alabugin, I. V.; Manoharan, M.; Peabody, S.; Weinhold, F. *J. Am. Chem. Soc.* **2003**, *125*, 5973–5987.
- (23) Buděšínský, M.; Fiedler, P.; Arnold, Z. *Synthesis* **1989**, 858–860.
- (24) Boldeskul, I. E.; Tsybal, I. F.; Ryltsev, E. V.; Latajka, Z.; Barnes, A. J. *J. Mol. Struct.* **1997**, *436/437*, 167–171.
- (25) van der Veken, B. J.; Herrebout, W. A.; Szostak, R.; Shchepkin, D. N.; Havlas, Z.; Hobza, P. *J. Am. Chem. Soc.* **2001**, *123*, 12290–12293.
- (26) Delanoye, S. N.; Herrebout, W. A.; van der Veken, B. J. *J. Am. Chem. Soc.* **2002**, *124*, 11854–11855.
- (27) Blatchford, M. A.; Raveendran, P.; Wallen, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14818–14819.
- (28) Yoshida, H.; Harada, T.; Ohno, K.; Matsuura, H. *Chem. Commun.* **1997**, 2213–2214.
- (29) Harada, T.; Yoshida, H.; Ohno, K.; Matsuura, H.; Zhang, J.; Iwaoka, M.; Tomoda, S. *J. Phys. Chem. A* **2001**, *105*, 4517–4523.
- (30) The conformation of an MDAE molecule $C_6H_3OC_6H_2C_2H_2N(C_6H_5)(C_6H_5)$ is designated using T (trans), G (gauche), and G' (torsion angle opposite to G) for the four bond axes $C_aO-C_bC_c$, OC_b-C_eN , $C_bC_c-NC_d$, and $C_bC_c-NC_e$ (see Figure 1). If these bonds assume, for example, T, G, T, and G' conformations, respectively, the conformation of the molecule or the conformer is designated as TG(T|G').
- (31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (32) For details, see the Supporting Information.
- (33) H^(g) denotes a hydrogen atom in the gauche' conformation with respect to the lone electron pair of the nitrogen atom.

JA030538F