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Shapes and Noncovalent Interactions of Oligomers: The Rotational Spectrum of the Difluoromethane Trimer

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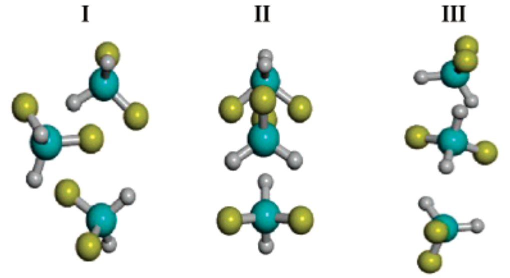
Abstract: The trimer of difluoromethane, $(CH_2F_2)_3$, has been characterized by supersonic jet Fourier transform microwave spectroscopy. The rotational spectrum displays all types (μ_a, μ_b, and μ_c) of transitions, showing that the adduct does not possess any element of molecular symmetry. The investigation of the three ^{13}C species in natural abundance indicates that the three carbon atoms form a triangle where the C−C distances are 3.648(2), 3.825(8), and 3.942(6) Å, respectively. The three subunits are held together by nine CH···F weak hydrogen bonds.

Introduction

Several homodimers have been studied by rotational spectroscopy, and precise information on their structures and on the nature of the forces that bind the monomers (M) have been obtained. Some of these dimers are linked together by hydrogen bonds, such as, for example, $(H_2O)_2$,[1] $[(CH_3)_2NH]_2$,[2] and $(CH_3OH)_2$.[3] The structure of $(H_2O)_2$[1] can be described only in a quantum-mechanical way, since it is vibrationally averaged over the multidimensional potential energy surface. Other dimers are linked by noncovalent CH···F and CH···O interactions, whose features have been investigated, e.g., through the studies of the dimers of difluoromethane[4] and dimethylether,[5] respectively. Finally, dispersion forces are primarily responsible for the formation of dimers such as $(CO_2)_2$[6] and $(C_6H_6)_2$.[7]

High-resolution spectroscopic studies of oligomers of the type M_n, with $n > 2$, can describe the gradual changes in properties in going from the monomer to the bulk. These kinds of studies are, however, very rare. Pure rotational spectra of homotrimers are available, indeed, only for two linear molecules, $(OCS)_3$[8] and $(HCN)_3$.[9] In addition, rotationally resolved far-infrared investigations of the trimers of the simplest (and very light) asymmetric rotor, water, have been reported, for the isotopic species $(H_2O)_3$[10] and $(D_2O)_3$.[11]

Table 1. Calculated Spectroscopic Constants and Energies [MP2 6-311++G(d,p)] of the Three Lowest Energy Conformers of $(CH_2F_2)_3$ Compared to the Experimental Values of the Parent Species



	exptl	I	II	III
A /MHz	1336.4	1380.1	1169.1	2272.0
B /MHz	820.5	843.1	853.6	458.7
C /MHz	592.7	611.2	603.9	413.1
$\|\mu_a\|$/D	strong	2.4	1.5	0.0
$\|\mu_b\|$/D	weak	0.6	0.1	0.6
$\|\mu_c\|$/D	weak	0.6	0.4	0.0
P_{cc}/uÅ^2	70.7	69.4	93.8	50.4
ΔE/kJ mol^{-1}	−	0(0)[a]	2.06(1.71)	5.90(5.45)

[a] Absolute energy −715.616 087 8 (−715.513 619 8) Ha. In parentheses the values with ZPE corrections.

Some years ago we studied the rotational spectrum of $(CH_2F_2)_2$,[4] the dimer of Freon 32, difluoromethane. Several lines were left unassigned in the Fourier transform rotational spectrum and could possibly be assigned to higher oligomers. Looking at the shape of the dimer in Chart 1a, it is evident that several sites are available for additional CH···F links. It is plausible to think that additional unities of the monomer can be attached to the dimer, forming, e.g., rings (Chart 1b) or chains (Chart 1c).

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(1) Fellers, R. S.; Leforestier, C.; Braly, L. B.; Brown, M. G.; Saykally, R. J. *Science* **1999**, *284*, 945.
(2) Tubergen, M. J.; Kuczkowski, R. L. *J. Chem. Phys.* **1994**, *100*, 3377.
(3) Lovas, F. J.; Belov, S. P.; Tretyakov, M. Y.; Stahl W.; Suenram, R. D. *J. Mol. Spectrosc.* **1995**, *170*, 4785.
(4) (a) Caminati, W.; Melandri, S.; Moreschini P.; Favero, P. G. *Angew. Chem., Int. Ed.* **1999**, *38*, 2924. (b) Blanco, S.; López, J. C.; Lesarri, A.; Alonso, J. L. *J. Mol. Struct.* **2002**, *612*, 255.
(5) Tatamitani, Y.; Liu, B.; Shimada, J.; Ogata, T.; Ottaviani, P.; Maris, A.; Caminati W.; Alonso, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 2739.
(6) Walsh, M. A.; England, T. H.; Dyke T. R.; Howard, B. J. *Chem. Phys. Lett.* **1987**, *142*, 265. Pine A. S.; Fraser, G. T. *J. Chem. Phys.* **1988**, *89*, 100.
(7) Arunan, E.; Gutowsky, H. S. *J. Chem. Phys.* **1993**, *98*, 4294.
(8) Ruoff, R. S.; Emilsson, T.; Klots, T. D.; Chuang, C.; Gutowsky, H. S. *J. Chem. Phys.* **1988**, *89*, 138.
(9) Peebles, R. A.; Kuczkowski, R. L. *J. Phys. Chem. A* **1999**, *103*, 6344.
(10) Keutsch, F. N.; Cruzan J. D.; Saykally, R. J. *Chem. Rev.* **2003**, *103*, 2533.
(11) Han, J.-X.; Takahashi, L. K.; Lin, W.; Lee, E.; Keutsch, F. N.; Saykally, R. J. *Chem. Phys. Lett.* **2006**, *423*, 344.

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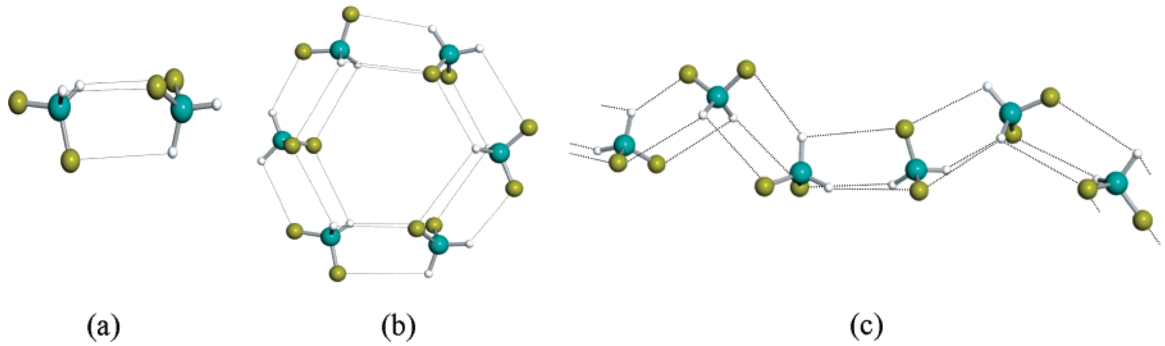
Chart 1. Plausible Oligomers of CH_2F_2, $(CH_2F_2)_n$[a]



[a] The dimer (a) has been observed by rotational spectroscopy.[4] Oligomers with higher *n*, either cyclic (b) or linear (c), could be stable forms. For the sake of simplicity, in (b) and (c) the symmetric forms are shown.

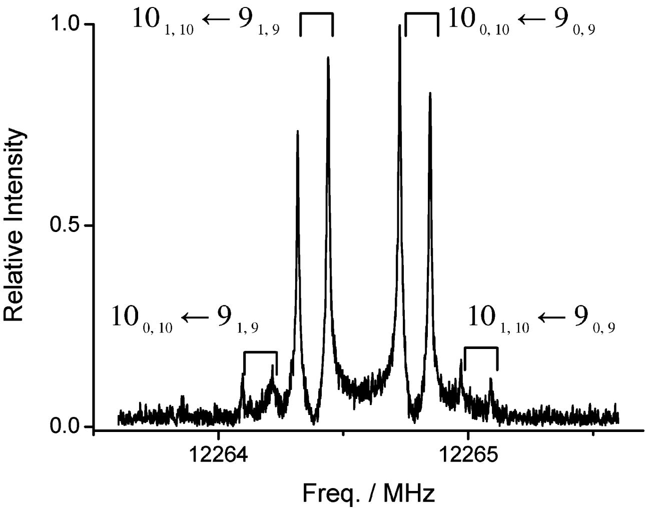


Figure 1. Portion of the rotational spectrum of $(CH_2F_2)_3$ for the parent species, showing a quartet of twin μ_a and μ_b lines. It was obtained collecting 100 cycles and with a excitation power of 0 dBm. Each component appears as a doublet (⊓) due to the Doppler effect.

Progressing in the study of the oligomers of CH_2F_2, after the dimer, we pursued the investigation of the rotational spectrum of the trimer, $(CH_2F_2)_3$. We present here the assignment of the pure rotational spectrum of the most stable form of $(CH_2F_2)_3$ and all of its singly substituted ^{13}C-isotopologues. Their analysis, individually and in combination, provides a wealth of evidence supporting a full asymmetry for its shape. The structural parameters of the carbon frame are derived quantitatively with high precision.

Methods

The rotational spectrum in the 6.5−18.0 GHz frequency region was measured using a coaxially oriented beam-resonator arrangement (COBRA)-type[12] pulsed supersonic-jet Fourier-transform microwave (FT−MW) spectrometer[13] described elsewhere,[14] recently updated with the FTMW++ set of programs.[15]

Table 2. Experimental Values of the Spectroscopic Parameters of the Most Abundant (Parent) and ^{13}C Isotopologues of $(CH_2F_2)_3$ (See Figure 2a for the Notation)

	parent[a]	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$
A/MHz	1336.3996(2)[b]	1323.7103(2)	1326.1132(2)	1336.3668(2)
B/MHz	820.5067(2)	818.2312(3)	817.8808(3)	814.8109(3)
C/MHz	592.678 70(5)	589.004 16(5)	589.259 83(5)	589.722 21(5)
P_{cc}/uÅ^2	70.698	70.708	70.680	70.718
σ/kHz[c]	2.1	2.9	2.8	3.6
N[d]	115	23	24	24

[a] The following centrifugal distortion constants have been determined for the normal species: $D_J = 0.4254(7)$ kHz, $D_{JK} = 1.384(2)$ kHz, $D_K = 1.746(4)$ kHz, $\delta_J = -0.0716(3)$ kHz, $\delta_K = 0.753(3)$ kHz. These values have been fixed in the parametric fits of the less abundant isotopologues. [b] Errors in parentheses are expressed in units of the last digit. [c] Standard deviation of the fit. [d] Number of transitions in the fit.

A gas mixture of 2% of CH_2F_2 in He at a total pressure of 2.0 bar was expanded through the solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry−Pérot cavity. The spectral line positions were determined after Fourier transformation of the 8k data points time domain signal, recorded with 100 ns sample intervals. Each rotational transition is split by Doppler effect due to the coaxial arrangement of the supersonic jet and resonator axes in the COBRA-FTMW spectrometer. The rest frequency is calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of frequency measurements is better than 3 kHz. Lines separated by more than 7 kHz are resolvable.

A commercial sample of CH_2F_2 (Aldrich) has been used without further purification. The spectra of the isotopic ^{13}C species have been measured in natural abundance.

Results, Analysis, and Discussion

To guide the assignment of the spectrum, ab initio calculations at a MP2 6-311++G(d,p) level[16] were performed for this system. Twelve "floppy" motions, which arise from the trimerization, have vibrational motions characterized by small forces: for this reason the convergence of the calculations was rather troublesome. However, several stationary points were found, whose configurations were dependent on the starting geometries of the trimer. Performing a frequency calculation in the harmonic approximation, we found conformers I−III, shown at the bottom of Table 1, to be the three stable ones. The corresponding sets of relative energies and spectroscopic constants are also collected in Table 1. In the table, P_{cc}, defined ahead in the text, represents, in a first approximation, the mass extension out of the CCC plane. We give, as Supporting

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(12) Grabow, J.-U.; Stahl, W. *Z. Naturforsch. A* **1990**, *45*, 1043. Grabow, J.-U. Doctoral thesis, Christian-Albrechts-Universität zu Kiel, Kiel, Germany, 1992. Grabow, J.-U.; Stahl, W.; Dreizler, H. *Rev. Sci. Instrum.* **1996**, *67*, 4072.

(13) Balle, T. J.; Flygare, W. H. *Rev. Sci. Instrum.* **1981**, *52*, 33.

(14) Caminati, W.; Millemaggi, A.; Alonso, J. L.; Lesarri, A.; Lopez, J. C.; Mata, S. *Chem. Phys. Lett.* **2004**, *392*, 1.

(15) Grabow, J.-U. 56th Ohio State University International Conference on Molecular Spectroscopy, MG01, Columbus, OH, 2001. Grabow, J.-U. Habilitationsschrift, Universität Hannover, Hannover, Germany, 2004; http://www.pci.uni-hannover.de/~lgpca/spectroscopy/ftmw.

(16) Frisch, M. J., et al. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

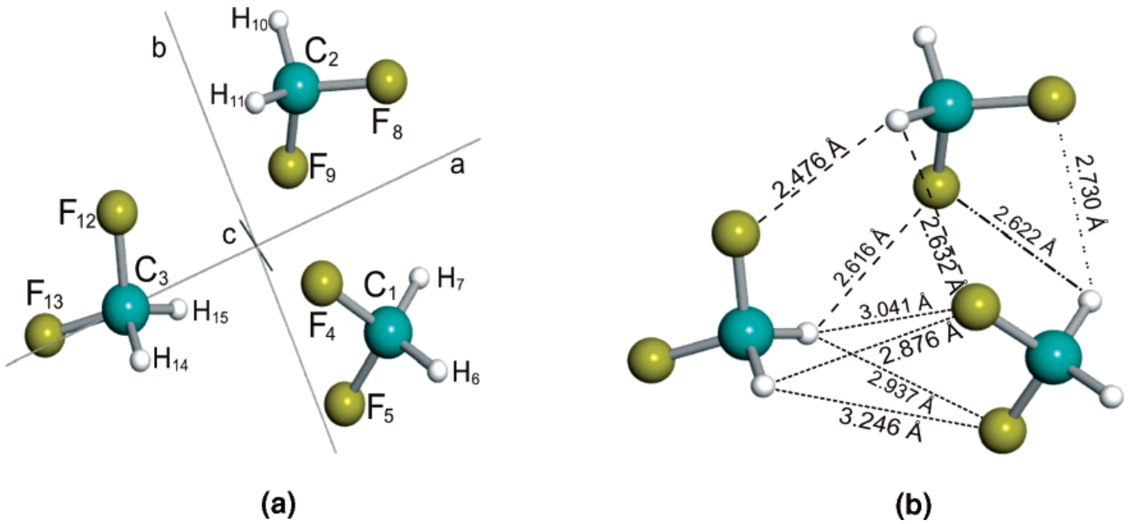

Figure 2. (a) Atom numbering and principal axis system; (b) the nine CH···F weak hydrogen bonds characterizing the cage structure of $(CH_2F_2)_3$.

Table 3. Substitution Coordinates (Å) and r_s Parameters (Å and deg) of the Triangle C1C2C3 of $(CH_2F_2)_3$ (See Figure 2a for the Labeling of Atoms and Principal Inertial Axis System)

(1) r_s coordinates are compared to the ab initio values of conformer I

	|*a*|/Å		|*b*|/Å		|*c*|/Å	
atom	r_s	ab initio	r_s	ab initio	r_s	ab initio
C_1	1.297 (1)[a]	1.314	1.911(1)	1.870	0.10(1)	0.141
C_2	1.406 (1)	1.367	1.728(1)	1.741	0.14(1)	0.059
C_3	2.0733(6)	2.076	0.10(1)	0.03	0.14(1)	0.069

(2) r_s structural parameters compared to the ab initio values of conformer I

	r_s	ab initio		r_s	ab initio
$r(C_1-C_2)$/Å	3.648(2)	3.617	∠C1−C2−C3/deg	60.4(1)	61.9
$r(C_2-C_3)$/Å	3.942(4)	3.874	∠C2−C3−C1/deg	56.0(2)	55.8
$r(C_3-C_1)$/Å	3.825(8)	3.860	∠C3−C1−C2/deg	63.6(2)	62.3

[a] Errors in parentheses in units of the last digit.

Information, (*i*) the tables with the Cartesian coordinates of the atoms of the three minima reported in Table 1; (*ii*) a table with energies and sketches of all found stationary points.

The μ_a- and μ_b-type transitions $J_{0,J} \leftarrow (J\text{-}1)_{0,J-1}$, $J_{1,J} \leftarrow (J\text{-}1)_{1,J-1}$, $J_{0,J} \leftarrow (J\text{-}1)_{1,J-1}$, $J_{1,J} \leftarrow (J\text{-}1)_{0,J-1}$, which appear as quartets (see Figure 1), were identified first and measured for several J quantum numbers. Then, a set of R-branch μ_a-, μ_b-, and μ_c-type transitions were measured for this conformer.

The observation of all three, μ_a-, μ_b-, and μ_c-type spectra, proves that the trimer does not possess any symmetry element, and for this reason conformer III of Table 1, belonging to symmetry group C_2, must be ruled out. The μ_a lines were more intense and required less microwave power to be optimized than the other two types of transitions (about 0 vs 10 dBm)

All measured lines (given as Supporting Information) could be fitted with the I^r representation of Watson's "A" reduced Hamiltonian.[17]

It was also possible to assign the spectra of the three ^{13}C isotopologues in natural abundance (≈ 1%); all spectroscopic constants are given in Table 2.

From the comparison of the experimental rotational constants with the ab initio values of Table 1, it is plausible to assign the observed spectrum to conformer I of Table 1. Extra data, such as the P_{cc} planar moment of inertia (see the values in Table 2) and the substitution coordinates[18] of the three carbon atoms (see Table 3) confirm this assignment. The estimated errors in r_S were calculated according to Costain's formula,[18b] $\delta z_i = 0.0012/|z_i|$ Å. These coordinates allow the C−C distances and angles of the triangle $C_1-C_2-C_3$, also listed in Table 3, to be obtained.

The planar moment of inertia P_{cc} $(= {}^1/_2(-I_{aa} + I_{bb} + I_{cc})$ gives the extension of the masses in the direction of the *c*-axis, that is, in a direction almost perpendicular to the CCC plane. Its value is 70.698 uÅ^2. The values of P_{cc} and P_{bb} of the monomer represent the extensions of the two hydrogens out of the FCF plane and of the two fluorines out of the HCH plane. Their values are 1.65 and 46.04 uÅ^2, respectively.[19] From these data we can roughly estimate that in the complex one monomer has two fluorine atoms in the CCC plane, one monomer has two hydrogen atoms in this plane, and the third monomer has an intermediate orientation. Moreover, all carbon atoms are close to the *ab* inertial plane. These considerations and the r_s coordinates of the three carbon atoms lead to the identification of the observed species with conformer I. This is also in agreement with the calculated values of the dipole moment components, and the relative intensities of the μ_a-, μ_b-, and μ_c-type transitions. For this conformer we obtained a plausible r_0

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(17) Watson, J. K. G. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: New York/Amsterdam, 1977; Vol. 6, pp 1−89.

(18) (a) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17. (b) Van Eijck, B. P. *J. Mol. Spectrosc.* **1982**, *91*, 348.

(19) Hirota, E. J. *Mol. Spectrosc.* **1978**, *71*, 145. Lide, D. R., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 3548.

Table 4. Twelve r_0 Fitted Parameters of $(CH_2F_2)_3$ Are Compared to the MP2/6-311++G(d,p) Values of Conformer I (See Figure 2a for Notation)

parameter	r_0	ab initio
$r(C_1-C_2)$/Å	3.635(3)[a]	3.617
$r(C_2-C_3)$/Å	3.878(3)	3.874
$\angle C_1-C_2-C_3$/deg	63.2(2)	61.9
$\angle F_4-C_1-C_2$/deg	57.1(4)	56.5
$\angle F_8-C_2-C_1$/deg	71.3(5)	68.2
$\angle F_{12}-C_3-C_2$/deg	52.3(5)	50.9
$\angle F_4-C_1-C_2-C_3$/deg	−57.4(5)	−57.2
$\angle F_5-C_1-F_4-C_2$/deg	−103.9(4)	−102.0
$\angle F_8-C_2-C_1-C_3$/deg	169.5(5)	170.3
$\angle F_9-C_2-F_8-C_1$/deg	−49.7(5)	−47.8
$\angle F_{12}-C_3-C_2-C_1$/deg	135.3(5)	134.9
$\angle F_{13}-C_3-F_{12}-C_{12}$/deg	−138.5(5)	−137.6

[a] Errors in parentheses in units of the last digit.

structure, determining the 12 parameters (see Figure 2 and Table 4) which give the positions of the three CH_2F_2 subunits with respect to each other.

To do this, we fit the 12 available rotational constants to obtain the 12 parameters. In the fit, we allowed these parameters to change, with respect to the MP2/6-311++G(d,p) ab initio values, in “confidence intervals” of 0.01 Å for the two bond distances and of 2° for the 10 intermonomers angles, according to the diagnostic least-square procedure described by Curl.[20] These structural parameters are reported in Table 4. The intramolecular parameters of each monomer have been kept fixed to the ab initio values, given as Supporting Information. The labeling for each atom is given in Figure 2a, where the shape of the trimer, according to its r_0 structure, is shown. In Figure 2b we indicate the nine CH···F interactions which stabilize this structure and their H···F distances, derived from the partial r_0 structure.

Since $(CH_2F_2)_3$ is cyclic, it has three times as many CH···F interactions as the dimer. The counterpoise corrected[21] dissociation energy for the trimer is calculated to be 17.8 kJ/mol, more than three times the dissociation energy of the dimer (5.4 kJ/mol[4]), suggesting some co-operative effects.

Conclusions

In this paper, we report the first pure rotational spectrum of a homotrimer of an asymmetric top molecule. We outline the trend and potentiality of rotational spectroscopy in giving precise information, beyond that on monomers and dimers, on trimers, and, hopefully, on larger oligomers. Moreover, it can supply detailed information on the chemical features of multiple weak hydrogen bonds,[22] a phenomenon which recently raised the interest of several researchers and which has been investigated with various techniques.[23−25]

Acknowledgment. This paper is dedicated to Dr. Rolf Meyer on the occasion of his 70th birthday. We thank the Ministero dell’Istruzione, dell’Università e della Ricerca (MIUR, PRIN 2004) and the University of Bologna (60% and funds for special topics) for financial support. S.B. thanks the Secretaría de Estado de Universidades e Investigación of the Ministerio de Educación y Ciencia of Spain and the University of Valladolid for financial support.

Supporting Information Available: Complete ref 16. Table 1s: the observed transition frequencies (ν, MHz) and differences between observed and calculated values ($\Delta\nu$, kHz)for the most abundant species of $(CH_2F_2)_3$. Table 2s: the observed transition frequencies (ν, MHz) and differences between observed and calculated values ($\Delta\nu$, kHz)for the ^{13}C species of $(CH_2F_2)_3$. Table 3s: MP2/6-311++G(d,p) structure of conformer I of $(CH_2F_2)_3$ (see Figure 2a for notation). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Curl, R. F. *J. Comput. Phys.* **1957**, *27*, 343.
(21) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(22) The weak hydrogen bond in structural chemistry and biology. *IUCr Monographs on crystallography*; Desiraju, G.R., Steiner, T., Eds.; Oxford University Press: 2001; Vol. IX.
(23) Delanoye, S. N.; Herrebout, W. A.; Van der Veken, B. J. *J. Am. Chem. Soc.* **2002**, *124*, 11854.
(24) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48.
(25) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.