Contribution to the Study of the Gauche Effect. The Complete Structure of the *Anti* Rotamer of 1,2-Difluoroethane

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The "gauche effect" characterizes the seemingly anomalous property of a *gauche* rotamer having a lower electronic energy than the corresponding *anti* rotamer.[1] An established example of the gauche effect is the relationship between the rotamers of 1,2-difluoroethane, where the *gauche* rotamer has a lower energy than the *anti* rotamer by 2.4−3.4 kJ/mol.[2,3] The rotamers of 1,2-dimethoxyethane are another example.[4] A corresponding anomaly, called the cis effect, exists in the energy relationship of the isomers of 1,2-difluoroethylene, 1,2-difluorodiazene and several other halogen- and oxygen-substituted ethylenes.[5] For these substances the *cis* isomer has the lower energy.

Through ab initio calculations, Wiberg and co-workers have investigated the gauche and cis effects.[6] Durig and co-workers and Muir and Baker have also done ab initio calculations which have given complete structures for the two rotamers of 1,2-difluoroethane.[3,7] Other workers have done extensive calculations to compare the *cis* and *trans* isomers of 1,2-difluoroethylene.[8] Wiberg has explained these effects in terms of a difference in bent-bond contributions to the σ part of the CC bond that *de*stabilizes the *anti* or *trans* species relative to the corresponding *gauche* or *cis* species. According to this model, the highly electronegative fluorine atom causes an increased *p* character in the C−F bond and thus a reduced angle between the carbon orbitals pointing toward the other carbon atom and the fluorine atom. Repulsion between the nonbonded atoms on each side of the CC bond causes tilting of the carbon orbitals away from the C−C axis. This tilting gives a more unfavorable overlap for the σ part of the CC bond for the *anti* or *trans* configuration than for the corresponding *gauche* or *cis* one.

Unavailable for discussions of the gauche effect has been an experimental structure of the *anti* rotamer of 1,2-difluoroethane. Because this rotamer lacks a dipole moment, its structure cannot be found by pure rotational spectroscopy in the microwave region. Also, electron diffraction studies gave no structural information on the *anti* rotamer[9,10] since the *gauche* rotamer is 85% or more of the mixture near room temperature. The principal subject of the present report is the application of high-resolution infrared spectroscopy to determining the complete structure of the *anti* rotamer.

Table 1. Principal Rotational Constants for the *Anti* Rotamer of 1,2-Difluoroethane and Its Isotopomers in the Ground State

	A^a	B^a	C^a
normal	1.057 385 7 (11)	0.129 390 34 (26)	0.120 654 86 (19)
$^{13}C_2$ species	1.022 404 2 (13)	0.128 804 08 (51)	0.119 686 28 (42)
d_4 species	0.690 217 8 (18)	0.125 291 66 (52)	0.115 473 98 (39)

^{a} In cm^{-1}. Statistical uncertainty in last two places given in parentheses.

Despite the dominance of the infrared spectrum of 1,2-difluoroethane by the *gauche* rotamer, one band in the spectrum is due almost entirely to the *anti* rotamer. This band, which arises from ν_{18} (b$_u$ symmetry species), the largely antisymmetric CCF bending mode, is centered at 284.260 cm^{-1} for the normal species and is principally B-type in character. The B-type component of this band, which also has a weaker A-type component, has been fully analyzed and recently reported.[11]

The corresponding B-type bands of the $^{13}C_2$ and d_4 rotamers have now been analyzed. These bands are centered at 279.941 and 264.257 cm^{-1}, respectively. To ground state combination differences (GSCD), Watson-type Hamiltonians were fitted.[12] For the $^{13}C_2$ species 1969 lines were assigned, and 1031 GSCDs were computed for use in the ground state fitting. For the d_4 species 1946 lines were assigned, and 1005 GSCDs were used. The A, B, and C rotational constants for the ground states of the three isotopomers are given in Table 1.

From a Chutjian−Nygaard-type, r_s analysis,[13] Cartesian coordinates were found for the carbon and hydrogen atoms in the *anti* rotamer. The CC and CH bond lengths and the CCH and HCH bond angles were computed. With these four parameters held at their r_s values, the CF bond length and the CCF angle were fitted to the full set of moments of inertia. This result is given in Table 2 and labeled r_s/r_0. In a separate analysis, all six of the molecular parameters were obtained in a global fitting to the nine experimental rotational constants. This result, labeled r_0 in Table 2, is little different from the r_s/r_0 one, which is preferred. The uncertainties are based on Costain estimates. The differences in the CC bond length and HCH bond angles by the two methods are a bit larger than expected and probably due to the influence of substantial anharmonicity of the d_4 substitution on the r_0 fitting. Table 2 also gives the geometric parameters for the *gauche* rotamer, which are r_0 values, as found from microwave spectroscopy.[14] The authors prefer the r_0 values over the r_s/r_0 values which are, however, little different.

Table 2 includes the results of the most recent ab initio calculations of geometric parameters done with hybrid HF-density functional methods.[7] Although the absolute values for the parameters differ some, the differences in parameters between the two rotamers are similar to those reported by Durig and co-workers from calculations with a 6-311++G** basis set.[3] With the exception of the larger change in the CF bond length, the changes in parameters between rotamers found in the experimental data are similar to those found in the ab initio calculations.

The principal adjustments in molecular parameters that occur in going from the *gauche* to the *anti* rotamer are in the CCF and CCH bond angles. The CCF bond angle decreases by 3.2°. One CCH bond angle changes negligibly, whereas the other increases by 3.1°. Thus, in the *gauche* rotamer, CFH moieties

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(1) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102.
(2) Huber−Wälchli, P.; Günthard, Hs. H. *Spectrochim. Acta* **1981**, *37A*, 285.
(3) Durig, J. R.; Liu, J.; Little, T. S.; Kalasinsky, V. F. *J. Phys. Chem.* **1992**, *96*, 8224.
(4) Connor, T. M.; McLauchlan, K. A. *J. Phys. Chem.* **1965**, *69*, 1888.
(5) For a summary, see Craig, N. C.; Piper, L. G.; Wheeler, V. L. *J. Phys. Chem.* **1971**, *75*, 1453.
(6) Wiberg, K. B. *Acc. Chem. Res.* **1996**, *29*, 229.
(7) Muir, M.; Baker, J. *Mol. Phys.* **1996**, *89*, 211.
(8) For a summary, see: Craig, N. C.; Brandon, D. W.; Stone, S. C.; Lafferty, W. J. *J. Phys. Chem.* **1992**, *96*, 1598.
(9) Friesen, D.; Hedberg, J. *J. Am. Chem. Soc.* **1980**, *102*, 3987.
(10) Fernholt, L.; Kveseth, K. *Acta Chem. Scand., Ser. A* **1980**, *34*, 163.

(11) Craig, N. C.; Klee, S.; Mellau, G. C.; Winnewisser, B. P.; Winnewisser, M. *J. Phys. Chem.* **1996**, *100*, 15049.
(12) Craig, N. C.; Abiog, A. P.; Hu, B.; Stone, S. C.; Lafferty, W. J.; Xu, L.-H. *J. Phys. Chem.* **1996**, *100*, 5310.
(13) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*, 3rd ed.; Wiley-Interscience: New York, 1984.
(14) Takeo, H.; Matsumura, C.; Morino, Y. *J. Chem. Phys.* **1986**, *84*, 4205.

Table 2. Experimental and Theoretical Geometric Parameters for the *Gauche* and *Anti* Rotamers of 1,2-Difluoroethane

	$r_{CH}{}^a$	$r_{CC}{}^a$	$r_{CF}{}^a$	$\alpha_{CCH}{}^b$	$\alpha_{HCH}{}^b$	$\alpha_{CCF}{}^b$	$\alpha_{FCH}{}^b$	method
				Experimental[c]				
gauche r_0	1.099(2)[d]	1.493(8)	1.390(3)	108.4(6)[d]	109.1(5)	110.6(5)	109.6(3)[d]	
	1.093(5)[e]			111.3(6)[e]			107.8(6)[e]	MW[f]
anti r_0	1.092	1.508	1.399	111.5	110.7	107.3	107.9	IR[g]
anti r_s/r_0	1.094(2)	1.501(4)	1.401(6)	111.4(2)	110.0(3)	107.4(5)	108.2(3)	IR[g]
				Theoretical				
gauche	1.093[d]	1.500	1.385	109.4[d]		111.0		
	1.092[e]			111.7[e]				calc[h]
anti	1.091	1.514	1.387	110.9		108.4	108.5	calc[h]

[a] Bond lengths in Å. [b] Angles in deg. [c] Uncertainties in last place in parentheses as reported in the microwave study and as estimated by the Costain method in the present work. [d] For the CH bond *gauche* relative to the CF bond on the other carbon atom. [e] For the CH bond *anti* relative to the CF bond on the other carbon atom. [f] Reference 14. [g] Present work. [h] Reference 7. As confirmed by the authors, the *gauche* and *anti* designations for CH bonds must be reversed to agree with the choice in ref 14.

which include the *gauche* CH bonds rotate approximately as a whole in the adjustment between the two rotamers. The CC and CF bonds are slightly longer in the *anti* rotamer with the difference being comparable to the sum of the uncertainties in the values for the two rotamers. In general, the differences between the *gauche* and *anti* rotamers of 1,2-difluoroethane are similar to the differences between the *cis* and *trans* isomers in 1,2-difluoroethylene.[12] The one exception is that the CC bond length appears to decrease in going from the *cis* to the *trans* isomer in 1,2-difluoroethylene.

How do the structural adjustments in going from the *gauche* to the *anti* rotamer relate to molecular features and to the Wiberg analysis?[6] The repulsion between neighboring CF bond moments in the *gauche* rotamer should cause an opening of the CCF bond angle in this rotamer. This adjustment is observed. Also consistent with repulsion of the CF bond moments, the FCCF dihedral angle in the *gauche* rotamer of 71.0(3)° is appreciably larger than the expected 60°.[14] The opposite sense of adjustment of the CCH bond angle is also consistent with the Wiberg analysis. In addition, the weakening of the CC bond in the *anti* rotamer due to less favorable overlap of the σ part of the bond should cause the CC bond to be longer in the *anti* rotamer, which is observed. On the other hand, the slightly longer CF bond in the *anti* rotamer does not seem to agree with the Wiberg model.

Samples of the $^{13}C_2$ and d_4 isotopomers were synthesized from commercial samples of 1,2-dibromoethane-$^{13}C_2$ and -d_4, respectively, by reaction with AgF_2.[11,12] Spectra were recorded on a Bruker IFS 120HR spectrometer with a resolution of less than 0.002 cm^{-1}. Pressures were in the range of 0.8 Torr, and path lengths in a White cell were 13 m. The Giessen Loomis-Wood program was helpful in making many of the subband assignments for these near prolate symmetric tops except for Q branches and strongly split R and P subbands with origins near the band center.[15] For the $^{13}C_2$ species, $\kappa = -0.9798$. For the d_4 species, $\kappa = -0.9658$. A modification of Arthur Maki's ASYM program was used in fitting Hamiltonians. For fitting the structural parameters the University of Michigan version of Richard Schwendeman's STRFIT program was employed.

JA963819E

(15) Winnewisser, B. P.; Reinstädler, J.; Yamada, K. M. T.; Behrend, J. *J. Mol. Spectrosc.* **1989**, *136*, 12.