Microwave Spectrum and Structure of the 3,5-Difluoropyridine $\cdots$ CO₂ van der Waals Complex

C. T. Dewberry,^(a) R. D. Cornelius,^(b) R. B. Mackenzie,^(c) C.J. Smith,^(c)
M. A. Dvorak,^(b) and K. R. Leopold^{(c),*}

Abstract

The rotational spectrum of the weakly bound complex 3,5-difluoropyridine $\cdots$ CO₂ has been observed using pulsed-nozzle Fourier transform microwave spectroscopy. Spectroscopic constants are reported for the parent and ¹³CO₂ isotopologues. The data indicate a planar structure in which the nitrogen approaches the carbon of the CO₂ with either a C_{2v} or effectively C_{2v} geometry in the ground vibrational state. The N $\cdots$ C van der Waals bond distance is 2.8245(16) Å and the oxygen $\cdots$ ortho-hydrogen distance is 3.091(2) Å. The N $\cdots$ C van der Waals bond length is 0.027(8) Å longer than that previously determined for pyridine–CO₂, but is still considerably shorter than the 2.998 Å distance in HCN $\cdots$ CO₂. M06-2X/6-311++G(3df,3pd) calculations place the binding energy of the complex at 4.3 kcal/mol (4.1 kcal/mol with counterpoise correction). The calculations further indicate that a secondary interaction between the ortho-hydrogens of the ring and the CO₂ oxygens account for ~50% of the total binding energy.

(a) Department of Chemistry and Biochemistry, Kettering University, 1700 University Avenue, Flint, MI 48504

(b) Department of Chemistry and Biochemistry, St. Cloud State University, 720 4th Avenue South, St. Cloud, MN 56301-4498

(c) Department of Chemistry, University of Minnesota, 207 Pleasant St., SE, Minneapolis, MN 55455

* E-Mail k Leopold@umn.edu; Tel.: (612) 625-6072; Fax.: (612) 626-7541

Keywords: Difluoropyridine; Microwave; Weakly Bound Complex; Carbon Dioxide Complex

Introduction

In a previous paper [1], we reported the microwave spectrum and structure of the complex formed from pyridine (py) and CO₂. The work was motivated by an earlier theoretical study [2] on the interaction between CO₂ and various nitrogen heterocycles which sought to guide the development of imidazolate and imidazolate based metal-organic frameworks (MOFs) for CO₂ capture. Further interest in the intermolecular interactions of CO₂ derives from its potential as an environmentally benign solvent [3,4].

The py-CO₂ complex was found to be planar with C_{2v} symmetry and with the nitrogen directed toward the CO₂ carbon. While this general structure was expected, the interesting observation was that the zero point N...C van der Waals distance of 2.7977(64) Å was anomalously short, having a value that was ~0.2 Å smaller than that found in CO₂ complexes with HCN [5] and NH₃ [6] (2.998 Å and 2.9875 Å, respectively). This result, together with the observed planarity of the complex was interpreted as an indication that the ortho-hydrogens of the pyridine are attracted to the CO₂ oxygen atoms, causing a decrease in the intermolecular separation and restricting the out-of-plane motion of the CO₂. The existence of such a secondary interaction was also discussed in the prior theoretical study [2].

In this work, we explore the interaction of CO₂ with 3,5-difluoropyridine. The structural and electronic effects of the fluorination of pyridine have been studied extensively by microwave spectroscopy [7,8] and the present work builds on those studies by exploring the effects of fluorination on intermolecular interactions with a neighboring moiety. Van Dijk *et al.* noted a measureable increase in electron density on the nitrogen of pyridine upon fluorination in the ortho positions, but observed no significant change with fluorine substitution in the meta positions [7,8]. These results were explained by a model which included resonance structures featuring donation of electron density from a lone pair on fluorine into the π system of the ring. With substitution in the ortho position, the resulting resonance structures place additional negative charge on the nitrogen atom, while substitution in the meta position puts increased electron density on the carbon adjacent to the nitrogen. In the latter case, such an effect could also alter the charge on the ortho-hydrogens and, in principle, influence the secondary hydrogen bonding interactions with the CO₂. Thus, in this paper, we examine the structure of the 3,5-

difluoropyridine...CO₂ complex by both microwave spectroscopy and computational methods in order to elucidate the effects of fluorine substitution in the meta positions of the ring.

Experimental Methods and Results

The rotational spectrum of 3,5-difluoropyridine...CO₂ was obtained using a Fourier transform microwave spectrometer with tandem cavity [9] and chirped-pulse [10] capabilities. Details of the instrument have been provided elsewhere [11,12]. Briefly, the cavity mode of the spectrometer operates along one axis and the chirped-pulse mode along an orthogonal axis. The nozzle introduces the molecular sample from a third axis perpendicular to both. Rapid switching between the two modes of operation is facilitated by an externally operated lever arm that introduces microwave absorbing foam between the cavity mirrors, thus suppressing ringing during the chirped-pulse experiments. Uncertainties in spectral line positions were ~60 kHz in the chirped-pulse spectra and ~4 kHz in the cavity spectra.

3,5-difluoropyridine was obtained from Fisher Scientific and chilled in a salted ice bath. A 1-2% gas mixture of CO₂ in Ar was bubbled through the liquid to entrain the vapor and the resulting mixture was expanded out of a pulsed nozzle at a stagnation pressure ranging between 1.3 and 3.4 atm. Initially, a chirped pulse spectrum from 6-18 GHz was taken using our standard circular 0.8 mm orifice nozzle, but the number of observed transitions was insufficient to make definitive spectral assignments. Using a newly developed 3D-printed nozzle that terminates in a 1.25" x 0.0085" slit [12], however, a sufficient number of rotational transitions were observed that spectral assignments could be made and an initial rough fit generated. Figure 1 shows a comparison between the chirped-pulse spectra with the traditional nozzle and the slit nozzle. Following the acquisition of the chirped-pulse spectrum, transitions were re-measured using the cavity system, and additional transitions were predicted and observed. (A simple 90 degree rotation of the slit nozzle allowed for its use in both the chirped pulse and cavity experiments.) A sample cavity spectrum is shown in Figure 2. ¹³CO₂ (Sigma-Aldrich – 99% ¹³C) was used to observe the isotopically substituted complex and spectra were collected in the same manner as the parent isotopologue.

For the parent isotopologue, transitions with frequencies ranging from 2900 – 9200 MHz were observed, while for the $^{13}\text{CO}_2$ species, spectra were recorded in the 2900 – 6600 MHz range. ^{14}N nuclear hyperfine structure was resolved for both isotopologues and the spectra were fit with the A-reduced Watson Hamiltonian [13] using the SPFIT program of Pickett [14]. Transition frequencies and assignments are provided in the supplementary material and spectroscopic constants are given in Table 1. No evidence of spectral doubling was observed, as would be expected if a barrier at the C_{2v} geometry gave rise to a pair of tunneling states associated with degenerate, asymmetric configurations.

Computational Methods and Results

M06-2X/6-311++G(3df,3pd) calculations were performed on the 3,5-difluoropyridine $\cdots\text{CO}_2$ complex using the Gaussian suite of programs [15]. Initially, the complex was assumed to have a planar, C_{2v} structure with the nitrogen of the pyridine directed toward the carbon of the CO_2 . At this structure, the N $\cdots$ C intermolecular bond distance is 2.715 Å (2.725 Å with counterpoise correction) and the binding energy is 4.3 kcal/mol (4.1 kcal/mol with counterpoise correction). It should be noted, however, that a frequency calculation revealed an imaginary frequency at the C_{2v} geometry, with a corresponding motion of an in-phase, in-plane intermolecular bending. Further investigation revealed a pair of degenerate, asymmetric minimum energy structures with the CO_2 bent slightly towards an ortho-hydrogen and a barrier at the C_{2v} structure of only 0.001 kcal/mol (with or without counterpoise correction). This barrier is quite small and is likely a computational artifact, but for reasons described below, no further calculations were performed to authenticate or refute its existence. The N $\cdots$ C bond distance and the complex binding energy are 2.717 (2.726) Å and 4.3(4.1) kcal/mole at the bent structure, where the numbers in parentheses are counterpoise corrected values.

For comparison, calculations were performed at the same level of theory for py- CO_2 , with the result that the N $\cdots$ C distance and binding energy are 2.689 (2.703) Å and 5.1 (4.8) kcal/mol, respectively. In this case, the C_{2v} structure corresponded to a true minimum on the potential energy surface. Comparison with the above results indicates that, at the level of theory used, fluorination of the pyridine ring in the 3 and 5 positions results in a slight increase in the N $\cdots$ C van der Waals bond length (~ 0.03 Å) and a slight decrease of ~ 0.8 kcal/mol in the binding

energy. Note that the computed N...C bond distance, 2.70 Å (with counterpoise correction), is in fair, though not excellent, agreement with the 2.7977(64) Å value determined experimentally [1]. While the MP2 calculations of Ref. [2] perform better, giving a value of 2.77 Å, the DFT-calculated 0.03 Å increase in van der Waals bond length between the pyridine and 3,5-difluoropyridine complexes is in excellent agreement with the 0.027(8) Å value determined experimentally (see below). This suggests that the present level of theory is suitable for drawing comparisons between the two systems. The counterpoise-corrected DFT binding energy of 4.8 kcal/mol reported here is in reasonable agreement with the MP2 values of Ref. [2], which lie in the 4.5 – 4.6 kcal/mole range (depending on basis set).

To estimate the contribution of the ortho-hydrogen...oxygen interactions to the total binding energy, CO₂ was rotated 90° out of plane at the C_{2v} structure, and a single point energy calculation was performed. The difference between the binding energies for the in-plane and out-of-plane CO₂ orientations in the C_{2v} geometry is 2.1 kcal/mol, suggesting that these “secondary” interactions, together, account for approximately 50% of the total interaction energy. Correspondingly, each ortho-hydrogen...oxygen interaction contributes ~1.05 kcal/mol to the total binding energy. A similar analysis of the CO₂...pyridine complex was carried out with the result that each ortho-hydrogen...oxygen interaction contributes ~1.10 kcal/mol to the total binding energy. This is similar to the 0.61 kcal/mol value obtained by Vogiatzis et al. [2] from MP2 calculations.

Population analysis at the M06-2X/6-311++G(3df,3pd) level was also performed in order to estimate the charges on atoms in both the pyridine and 3,5-difluoropyridine monomers. Several methods, including NPA [16], ESP [17], and Hirschfeld [18] analyses, were employed. The results for key atoms of interest are displayed in Figure 3. The computed value of the component of the dipole moment of 3,5-difluoropyridine...CO₂ along its *a*-inertial axis is 1.46 D [19].

Analysis of Spectroscopic Constants

The inertial defect of the complex,

$$\Delta_{ID} = \frac{h}{8\pi^2} \left(\frac{1}{C} - \frac{1}{A} - \frac{1}{B} \right) \quad (1)$$

calculated from the fitted rotational constants, is 0.29 amu Å² for the parent species (0.30 amu Å² for the ¹³CO₂ isotopologue). These values are small and therefore indicative of a planar system. Although out-of-plane vibrations should render the value negative, it is not uncommon for truly planar systems to have slightly positive inertial defects. Indeed, it is interesting to note that Δ_{ID} of the 3,5-difluoropyridine monomer, which is certainly planar, has a value of 0.056 amu Å². In this light, and in view of the planar geometry determined computationally, a planar structure for the complex is assumed in the analysis of the rotational constants. Moreover, in the absence of any evidence of tunneling, we assume that the small barrier calculated at the C_{2v} structure is either a computational artifact or is sufficiently far below the zero point level that the complex can be treated as having an effective C_{2v} geometry in the ground vibrational state.

A diagram illustrating the overall geometry and the relevant structural parameters is given in Figure 4. Structural parameters for the 3,5-difluoropyridine monomer have been determined for the six-membered ring [7], but the fluorine and hydrogen positions have not been obtained experimentally. Thus, we sought to determine the van der Waals bond distance in the complex, $R(N\cdots C)$, by a method which did not explicitly require knowledge of the fluorine and hydrogen coordinates. This was accomplished as follows: First, the separation between centers of mass of the monomers (R_{cm}) was determined for each isotopologue from the C rotational constant. For a planar system, this calculation is independent of the angular orientation of the monomer units and, by the parallel axis theorem, is readily accomplished using the relation

$$I_{cc} = \mu R_{cm}^2 + I_{bb}^{CO_2} + I_{cc}^{DFP} \quad (2)$$

Here, I_{cc} is the vibrationally averaged moment of inertia of the complex about its c -inertial axis, μ is the pseudodiatom reduced mass, and the second and third terms are the indicated zero point moments of inertia of CO₂ [20] and 3,5-difluoropyridine [7], respectively.

To determine the van der Waals bond length, the distance between the nitrogen atom and the center of mass of the 3,5-difluoropyridine, r_{cm} , was subtracted from R_{cm} . The determination of $r_{cm} = 1.7987(14)$ Å was accomplished by a separate Kraitchman analysis of the rotational constants for 3,5-difluoropyridine and its ^{15}N isotopologue reported by van Wijngaarden and coworkers [7]. The results for $R(N\cdots C)$ of the parent and $^{13}\text{CO}_2$ isotopologues were in excellent agreement, with values of $2.8246(14)$ Å and $2.8243(14)$ Å, respectively and an average value of $2.8245(16)$ Å [21]. These distances reproduce the observed values of A and B to within 1.9 MHz and 123 kHz, respectively for both isotopologues. (The method guarantees exact agreement with the value of C .) Using the average value of $R(N\cdots C)$, and the individual monomer structures for CO_2 and 3,5-difluoropyridine, the distance between the CO_2 oxygen and its nearest ortho-hydrogen in the complex is determined to be $3.091(2)$ Å [22]. The intermolecular structural parameters are summarized in Table 2, where they are also compared with previously determined values for the pyridine $\cdots\text{CO}_2$ complex.

An estimate of the zero point bending vibrational amplitude of the 3,5-difluoropyridine (θ in Figure 4) was made from the observed ^{14}N nuclear hyperfine structure. Invoking the usual assumption that the electronic structure of the 3,5-difluoropyridine is negligibly perturbed by the weak intermolecular interaction, the observed value of χ_{aa} of the complex is related to the angle θ , formed between the principal axis system of the quadrupole coupling tensor of free 3,5-difluoropyridine and the inertial axis system of the complex

$$\langle \chi_{aa} \rangle = \chi_{bb}^o \langle \cos^2 \theta \rangle + \chi_{aa}^o \langle \sin^2 \theta \rangle \quad (3)$$

Here, χ_{gg}^o represents the quadrupole coupling constant of free 3,5-difluoropyridine along its g -inertial axes, and the angular brackets denote vibrational averaging. This equation recognizes that the eigenvectors of the quadrupole coupling tensor of free 3,5-difluoropyridine are aligned with its inertial axis system (by symmetry) and that its a -axis is perpendicular to the C_2 axis. Values of $\chi_{aa}^o = 1.15163$ MHz, $\chi_{bb}^o = -5.0350$ MHz were taken from previously published work [7]. Using the values of χ_{aa} given in Table 1, values of $\theta_{eff} = \cos^{-1}(\langle \cos^2 \theta \rangle^{1/2}) = 8.8^\circ$ and 9.0° are obtained for the parent and $^{13}\text{CO}_2$ species, respectively. It should be noted, however, that

employing previously derived equations for the inertial tensor components of a binary complex [23], the value of $\theta_{eff} = 8.8^\circ$ gives somewhat poorer agreement between observed and calculated rotational constants for the parent species than the 1.9 MHz and 123 kHz values for A and B quoted above. Indeed, for the parent species, the best agreement between observed and calculated B rotational constant is found when $\theta_{eff} = 1.86^\circ$, with B reproduced to within 1 kHz. Optimum agreement with the A rotational constant is found at $\theta_{eff} = 2.93^\circ$. The disparity between θ_{eff} determined from analysis of hyperfine constants and that obtained from rotational constants may result from slight perturbation of the electric field gradient at the nitrogen nucleus upon complexation.

With R_{cm} determined and θ_{eff} estimated from either hyperfine structure or observed rotational constants, it is possible, in principle, to use either I_{aa} or $(I_{bb} + I_{cc})$ to estimate the amplitude of the CO_2 angular oscillations about the perpendicular geometry (γ_{eff} in Fig. 4). In the pyridine- CO_2 complex, a value of $\gamma_{eff} = 2.4^\circ$ was obtained from I_{aa} using the value of θ_{eff} determined from hyperfine structure. In the present case, however, similar calculations using $\theta_{eff} = 8.8^\circ$ and either I_{aa} or $(I_{bb} + I_{cc})$ yield values of $\langle \cos^2 \gamma \rangle$ slightly greater than one. Reducing θ_{eff} to 1.86° (the value that best reproduces B) gives values of $\langle \cos^2 \gamma \rangle = 0.98905$ ($\gamma_{eff} = 6.0^\circ$) or 1.00000 ($\gamma_{eff} = 0.0^\circ$) from I_{aa} or $(I_{bb} + I_{cc})$, respectively [24]. While the 6° value is not unreasonable, it should be noted that the moments of inertia of the complex depend very weakly on γ and thus, its influence is likely buried beneath that of the same vibrational effects that give rise to the slightly positive inertial defect. In other words, in pyridine- CO_2 , the inertial defect was small and negative, whereas in the 3,5-difluoropyridine- CO_2 , it is small and positive. This indicates a slight contamination of the experimental rotational constants by untreated vibrational effects in the present case and suggests that these effects may obscure the dependence of the experimental rotational constants on γ (thus accounting for the unphysical and variable values of $\langle \cos^2 \gamma \rangle$ obtained). Overall, the weak dependence of the moments of inertia of the complex on γ , combined with the difficulty associated with the underlying assumption of equation 3, render it difficult to accurately assess the angular vibrational amplitudes of the two moieties. At best, we estimate that θ_{eff} is between $\sim 2^\circ$ and 9° and that γ_{eff} is “small” (perhaps a few degrees). Fortunately, these issues have no significant effect on the reported value of $R(N \cdots C)$.

Discussion

Fluorination at the 3 and 5 positions of the pyridine ring in py-CO₂ results in an increase in the N...C zero point averaged van der Waals bond length of 0.027(8) Å. A similar change of 0.03 Å is predicted for the equilibrium bond length by DFT calculations. The distance between the CO₂ oxygens and their nearest ortho-hydrogen, 3.091(2) Å, is very similar to the 3.048 Å value in py-CO₂ [25] despite the increased van der Waals distance. The increase in the length of the N...C van der Waals bond, and the slightly lower binding energy of the complex relative to that of py-CO₂ (4.8 kcal/mol for the pyridine complex vs. 4.1 kcal/mol for the 3,5-difluoropyridine complex) are indications that the binding of CO₂ to 3,5-difluoropyridine is slightly weaker than that to pyridine. The N...C van der Waals bond length (2.8245 Å) lies between those of pyridine-CO₂ (2.7977 Å) and HCN-CO₂ (2.9875 Å), but is much closer to that of pyridine-CO₂.

While it is difficult to unambiguously identify the cause of the increase in van der Waals bond length upon 3,5-fluorination of the pyridine ring, some insight can be gained by taking a closer look at the electronic structure of the aromatic moiety in the two systems. The population analysis summarized in Figure 3 shows that, according to all methods of calculation used, the charge on nitrogen is slightly less negative in 3,5-difluoropyridine compared with pyridine. As the difference is small, it is not necessarily inconsistent with the analysis of nuclear hyperfine structure given in reference [7], which indicated little or no change in the charge on the nitrogen upon fluorination in the meta position [26]. Even such a small difference, however, would presumably decrease the Lewis basicity of the nitrogen atom and give rise to a longer intermolecular N...C distance. The population analysis also confirms an increase in negative charge on the ortho- carbon (or decrease in positive charge), as predicted [7,8], as well as an increased positive charge on the ortho-hydrogens. The latter, as noted above, should strengthen the secondary interaction with CO₂ oxygen atoms (though the slight increase in the O...H distances upon fluorination indicated in Table 2 would mitigate this effect to some degree.) How the competing effects of fluorine substitution on the Lewis basicity of the nitrogen and on the positive charge on the ortho-hydrogens play out is not necessarily obvious *a priori*, but the evidence would suggest that its influence on the nitrogen is, if not the sole effect, at least the dominant one.

Conclusion

The microwave spectrum of the 3,5-difluoropyridine $\cdots$ CO₂ complex has been observed in a supersonic jet. The system is planar and has a C_{2v} or effectively C_{2v} structure in the ground vibrational state. In the zero point vibrationally averaged geometry, the C_2 axis of the difluoropyridine is perpendicular to the CO₂, with the nitrogen directed toward the carbon. Analysis of the observed rotational constants indicates that the N $\cdots$ C weak bond distance and the O $\cdots$ ortho-H secondary hydrogen bond distance, 2.8245(16) Å and 3.091(2) Å respectively, are slightly longer than those previously observed in pyridine-CO₂. These results are consistent with our computational work. The N $\cdots$ C van der Waals bond length lies between those previously determined for pyridine $\cdots$ CO₂ and HCN $\cdots$ CO₂, but much closer to that of the pyridine complex. The binding energy of 3,5-difluoropyridine-CO₂ obtained from M06-2X/6-311++G(3df,3pd) calculations, is slightly smaller than that of the pyridine complex (4.1 vs. 4.8 kcal/mole with counterpoise corrections, respectively). Overall, the fluorination of pyridine in the 3 and 5 positions appears to slightly weaken its interaction with CO₂. The secondary hydrogen bonding interactions remain intact, however, and the system is held in a planar configuration.

Acknowledgments

This work was supported by the National Science Foundation (Grant Nos. CHE-1266320 and CHE-1563324), the St. Cloud State University Office of Sponsored Programs, St. Cloud State University College of Science and Engineering, and by an NSF REU Research Fellowship awarded to R.D.C. through the University of Minnesota. We are grateful to Professor Steven Kass for helpful discussions.

Appendix A. supplementary material

Supplementary data associated with this article can be found in the online version, at <http://xxxxxx>

References

---

1. J.L. Doran, B. Hon, K.R. Leopold, *J. Mol. Struct.* 1019 (2012), 191.
2. K.D. Vogiatzis, A. Mavrandonakis, W. Klopper, G.E. Froudakis, *ChemPhysChem.* 10 (2009) 374.
3. P. Raveendran, Y. Ikushima, S.L. Wallen, *Acc. Chem. Res.* 38 (2005) 478.
4. K.H. Kim, Y. Kim, *J. Phys. Chem. A* 112 (2008) 1596.
5. K.R. Leopold, G.T. Fraser, W. Klemperer, *J. Chem. Phys.* 80 (1984) 1039.
6. G.T. Fraser, K.R. Leopold, W. Klemperer, *J. Chem. Phys.* 81 (1984) 2577.
7. C.W. van Dijk, M. Sun, J. van Wijngaarden. *J. Mol. Spectrosc.* 280 (2012) 34.
8. C.W. van Dijk, M. Sun, J. van Wijngaarden, *J. Phys. Chem. A* 116 (2012) 4082.
9. T.J. Balle, W.H. Flygare, *Rev. Sci. Instrum.* 52 (1981) 33.
10. G.G. Brown, B.C. Dian, K.O. Douglass, S.M. Geyer, S.T. Shipman, B.H. Pate, *Rev. Sci. Instrumen.* 79 (2008) 053103.
11. J.A. Phillips, M. Canagaratna, H. Goodfriend, A. Grushow, J. Almlöf, K.R. Leopold *J. Am. Chem. Soc.* 117 (1995) 12549.
12. C.T. Dewberry, R.B. Mackenzie, S. Green, K.R. Leopold, *Rev. Sci. Instrum.* 86 (2015) 065107.
13. W. Gordy, R.L. Cook, *Microwave Molecular Spectra*, Third Ed., John Wiley and Sons, New York, 1984.
14. H.M. Pickett, *J. Mol. Spectrosc.* 148 (1991) 371.
15. Gaussian 09, Revision **E.01**, 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
16. J.P. Foster, F. Weinhold, *J. Am Chem. Soc* 102 (198) 7211.
  17. U. C. Singh and P. A. Kollman, *J. Comp. Chem.*, 5 (1984) 129.
  18. F. L. Hirshfeld, *Theor. Chem. Acc.*, 44 (1977) 129.
  19. This value applies to either the C_{2v} or the bent geometry. The dipole moment component along the b -inertial axis in the latter case is calculated to be only 0.01 D.
  20. L.S. Rothman and L.D.G. Young, *J. Quant. Spectrosc. Radiat. Transfer* 25 (1981) 505.
  21. Note that these errors are not statistical and thus the quoted uncertainty is chosen to encompass the maximum and minimum values implied by the error bars on the individual determinations.
  22. This calculation requires knowledge of the ortho C-H distance and the NCH bond angle, neither of which are known experimentally for 3,5-difluoropyridine. Thus, to compute the O $\cdots$ H distance, the differences between the M06-2X/6-311++G(3df,3pd) values for pyridine and 3,5 difluoropyridine were imposed on the experimental values for the pyridine monomer. The quoted error bar corresponds only to that in the N $\cdots$ C van der Waals bond length.
  23. K.R. Leopold, *J. Mol. Spectrosc.* 2012, 278, 27-30. E: *J. Mol. Spectrosc.* 2013, 293, 60.
  24. Using the 2.93° value that optimizes A also yields values of $\langle \cos^2 \theta \rangle$ slightly greater than one.
  25. Reference 1 quotes a value of 3.090 Å. The 3.048 Å quoted here is a corrected value which removes a small calculational error in the previous determination.
  26. Although simple resonance structures involving π -electron donation by the fluorines place no additional charge on the nitrogen atom, a small increase in negative charge may still be expected to result from donation of electron density to the ring. In this light, the near invariance of the nitrogen charge upon meta-fluorination is consistent with an approximate cancellation of σ electron withdrawal and π electron donation. However, since the lone pair on the nitrogen is part of the σ framework of the molecule, a decrease in Lewis basicity is not necessarily inconsistent with the invariance of atomic charge upon meta fluorination.

Table 1: Spectroscopic Constants of the 3,5-Difluoropyridine...CO₂ Complex^a

	3,5-DFP... ¹² CO ₂	3,5-DFP... ¹³ CO ₂
<i>A</i> (MHz)	1550.4396(27)	1550.4573(61)
<i>B</i> (MHz)	622.74643(24)	614.37585(57)
<i>C</i> (MHz)	444.17854(13)	439.90179(34)
χ_{aa} (MHz)	-4.8803(33)	-4.876(13)
$(\chi_{bb} - \chi_{cc})$ (MHz)	-1.865(14)	-1.871(19)
Δ_J (kHz)	0.1070(17)	0.1058(53)
Δ_{JK} (kHz)	2.938(25)	2.879(47)
δ_K (kHz)	1.847(41)	1.75(12)
δ_J (kHz)	0.02960(85)	0.0327(31)
<i>N</i> ^b	85	39
Δ_{ID} (amu Å ²)	0.292	0.301
RMS (kHz)	2	2

^a Numbers in the parentheses are one standard error in the least squares fit.^b Number of transition frequencies in the least squares fit.

Table 2: Summary of Experimental and Theoretical Results^a

	3,5-difluoropyridine...CO₂^b			pyridine...¹²CO₂^{a,c}
Parameter	¹²CO₂	¹³CO₂	M06-2X/6-311++G(3df,3pd)^e	
R_{cm} [Å] ^d	4.623342(1)	4.623048(3)	4.50(4.51)	4.19269
$R(N\cdots C)$ [Å]	2.8246(14)	2.8243(14)	2.715(2.725)	2.7977(64)
θ_{eff} [deg]	8.8 ^f	9.0 ^f	-	9.0
$R(ortho-H\cdots O)$ [Å]	3.091(2)	3.090(2)	2.99(2.99)	3.048(6)
ΔE [kcal/mol]	-	-	4.3(4.1)	4.9 ^{b,g}

(a) Experimental values unless otherwise indicated. (b) This work. (c) Reference [1]. (d) Obtained using the value of $r_{cm} = 1.7987(14)$ Å for 3,5-difluoropyridine. (e) Calculated at the C_{2v} structure. Counterpoise corrected values in parentheses. (f) Value determined from nuclear hyperfine structure. A value of 1.86° gives somewhat better agreement with the observed values of A and B for the parent species. See text for discussion. (g) Also obtained using M06-2X/6-311++G(3df,3pd) calculations.

Figure Captions

Figure 1. Chirped pulse spectrum of a mixture of 3,5-difluoropyridine and CO₂ as described in the text. The top spectrum was taken using a 1.25" x 0.0085" slit nozzle. The boxed transition of 3,5-difluoropyridine–CO₂ was not observed in the bottom spectrum, which was taken with a standard circular nozzle. Both spectra represent the average of 10,000 free induction decay signals and are displayed on the same vertical scale.

Figure 2. Cavity spectrum showing the $8_{08} \leftarrow 7_{07}$ transition of 3,5-difluoropyridine⋯CO₂ with clearly resolved ¹⁴N nuclear hyperfine structure. From left to right, *F* assignments are $8 \leftarrow 7$, $7 \leftarrow 6$, and $9 \leftarrow 8$. The spectrum was produced from averaging 1800 free induction decay (FID) signals at 4 free induction decay signals per gas pulse.

Figure 3: Results of M06-2X/6-311++G(3df, 3pd) population analyses for pyridine and 3,5 – difluoropyridine. Grey = pyridine; Black = 3,5-difluoropyridine

Figure 4. A representation of the 3,5-difluoropyridine⋯CO₂ complex indicating the center of mass distance (R_{cm}), the distance between the nitrogen atom and the center of mass of the 3,5-DFP (r_{cm}) and the N⋯C van der Waals distance ($R(N\cdots C)$). Large amplitude bending vibrations of the 3,5-difluoropyridine and CO₂ away from the C_{2v} geometry are denoted by θ and γ , respectively.

Figure 1

Figure 2

Figure 3

Figure 4

TOC Graphic