Charge Distributions and Isomer Stability of the Fluoro Derivatives of Methylenimide

James M. Howell

Contribution from the Department of Chemistry, Brooklyn College, City University of New York, Brooklyn, New York 11210.

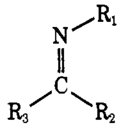
Received April 2, 1975

Abstract: Geometry optimized STO-3G calculations have been performed on $CH_2{=}NH$, and its seven fluoro derivatives. The energies of the different fluoro derivatives are correlated with the charge distribution in the parent system. The cis isomer of $CHF{=}NF$ is calculated to be of lower energy than the trans, similar to the situation for $NF{=}NF$ and $NH{=}NH$.

$CH_2{=}NH$ is intermediate in structure between the isoelectronic molecules $CH_2{=}CH_2$ and $NH{=}NH$. The effect of fluorine substitution is unusual in this series since, for $NF{=}NF$[1] and $CHF{=}CHF$,[2] the cis isomer is of lower energy than the trans. The halogen derivatives of CH_2NH have been observed[3-8] and semiempirical[9] as well as ab initio calculations[10] without geometry optimization performed on the monofluoro derivatives.

We report geometry optimized calculations at the minimal STO-3G level[11] for CH_2NH and its seven different fluoro derivatives.

Structure **1** defines the numbering system. Table I gives the energies of the various molecules along with their overall Mulliken population data, while Table II gives the optimized geometries. In particular, it should be noted that, for the parent species, the positive charge on the hydrogens decreases in the order



1

$$\text{H1 } (0.151) > \text{H3 } (0.073) > \text{H2 } (0.060)$$

which correlates with the energies of the different monofluoro isomers (relative energies in kcal/mol)

$$\mathbf{3}\ (45.2) > \mathbf{5}\ (3.8) > \mathbf{4}\ (0.0)$$

The 1,2-difluoro derivatives show similar trends. Structures **7** and **8** are lower in energy than **6**. Furthermore, the cis isomer, with $R2 = F$, is of slightly lower energy than the trans isomer. This result completes the isoelectronic series NFNF, CHFNF, and CHFCHF, where the cis isomer is of lower energy. The cis–trans energy difference of CHFNF should probably be larger as the ab initio calculations seem to put the energy of the cis isomer at slightly too high an energy relative to that of the trans. For instance, geometry optimized STO-3G calculations of N_2F_2 put the energy of the cis form at only 0.1 kcal/mol lower than that of the trans form compared with the experimental value of 3 kcal/mol (STO4-31G favors c-N_2F_2 by about 1.0 kcal/mol). Similarly, geometry optimized STO-3G calculations of 1,2-difluoroethylene erroneously put the energy of the trans form slightly lower than that of the cis isomer, whereas the reverse is found experimentally.[2]

In our calculations[12] on N_2F_2, we partially attributed the lower energy of the cis isomer to the different charge distribution in the isomers. The cis isomer puts more electron density on the fluorine atoms than does the trans. As explained above, the same effect seems to hold for the CH_2NH derivatives.

The variations of charge distributions with site may lie in hyperconjugative effects. For instance, in $CH_2{=}NH$, the C—H2 overlap population is somewhat smaller than for the C—H3 bond. Additionally when $R2 = R3$ it is found that R2 is more negative than R3. These results are as would be expected for a stronger hyperconjugative donation of the nitrogen lone pair into the C-R2 σ^* bond than occurs into the C-R3 σ^* bond. Since hyperconjugation would be better to a C-F σ^* bond than to a C-H σ^* bond, an argument could be constructed on the basis of hyperconjugation to rationalize the site preferences. However, we are hesitant to accept hyperconjugation as the sole, decisive factor in determining the energies of the different isomers. If hyperconjugation were dominant, we would expect that the C=N overlap population would be higher (and the bond length shorter) in **4** than in **5** and in **8** than in **7**. This is the case for the former pair but not the latter. For a further discussion of related points, see ref 12. It appears that hyperconjugation may favor charge buildup on R2 preferentially to R3 but that the preference of fluorine for sites of high electron density is also needed to explain the site preference.

It is interesting to see how far charge distributions can go to explain preferred sites for fluorine atoms. Radom, Hehre, and Pople have calculated the energies of different isomers and rotamers of fluorinated compounds. For instance, the preferred site of fluorine in the substituted gauche hydrazine NH_2NHF is in the "internal" position.[13] If reference is made to the compilation of ab initio molecular orbital results by Snyder and Basch,[14] it is found that, for the parent system N_2H_4, the "internal" hydrogens are more negative than the "external" (+0.261 vs. +0.308).

Furthermore, one may compare the charge distributions for CH_3OH and CH_3NH_2 calculated by Hehre and Pople[15] with the rotational barrier of the fluorinated derivatives described later by Radom, Hehre, and Pople.[13] Both parent molecules were calculated in staggered geometries and Mulliken charges obtained. When fluorine substitution was made, the low energy conformer was the one putting the electronegative F atom at the site occupied by the most negative hydrogen atom in the parent molecule.

Acknowledgment. This work was supported in part by a grant from the Faculty Research Award Program of the City University of New York. A generous grant of computer time from the Central Computer Facility of CUNY is acknowledged. We are grateful for valuable discussions with N. D. Epiotis of the University of Washington.

Table I. Molecular Energies and Mulliken Population Analysis for $CH_2{=\!=}NH$ and Fluorine Derivatives

Molecule					Gross charges					Overlap population			
	R1	R2	R3	Energy	C	N	R1	R2	R3	C=N	N—R1	C—R2	C—R3
2	H	H	H	−92.82303	−0.009	−0.276	0.151	0.060	0.073	1.040	0.622	0.770	0.777
3	F	H	H	−190.26001	−0.034	−0.081	−0.069	0.088	0.096	0.979	0.345	0.781	0.767
4	H	F	H	−190.29267	0.195	−0.308	0.159	−0.133	0.087	1.020	0.622	0.453	0.756
5	H	H	F	−190.28952	0.201	−0.310	0.161	0.070	−0.122	1.009	0.631	0.744	0.465
6	H	F	F	−287.76289	0.399	−0.333	0.170	−0.126	−0.110	0.979	0.631	0.438	0.456
7	F	H	F	−287.71884	0.182	−0.115	−0.061	0.096	−0.102	0.940	0.345	0.743	0.466
8	F	F	H	−287.72019	0.176	−0.114	−0.060	−0.107	0.106	0.940	0.342	0.456	0.760
9	F	F	F	−385.18510	0.389	−0.140	−0.053	−0.102	−0.094	0.896	0.340	0.443	0.457

Table II. STO-3G Optimized Geometries for $CH_2{=\!=}NH$ and Fluorine Derivatives

Molecule				Bond lengths, Å				Bond angles, deg		
	R1	R2	R3	C=N	N—R1	C—R2	C—R3	R1—N—C	R2C—N	R3—C—N
2	H	H	H	1.274	1.049	1.091	1.089	109	125	119
3	F	H	H	1.287	1.377	1.089	1.085	110	124	118
4	H	F	H	1.272	1.048	1.351	1.096	108	125	121
5	H	H	F	1.274	1.045	1.101	1.346	108	127	120
6	H	F	F	1.275	1.045	1.353	1.341	107	126	123
7	F	H	F	1.291	1.378	1.098	1.344	109	125	120
8	F	F	H	1.291	1.379	1.347	1.094	110	124	119
9	F	F	F	1.296	1.381	1.348	1.340	109	126	122

References and Notes

(1) G. T. Armstrong and S. Marantz, *J. Chem. Phys.*, **38**, 169 (1962); see also J. Binenboym, A. Burcat, A. Lifshitz, and J. Shamir, *J. Am. Chem. Soc.*, **88**, 5039 (1966).
(2) H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960); see also W. A. Sheppard and C. M. Shartz, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969.
(3) (a) S. P. Markov, A. Ya. Yakubovich, A. S. Filatov, M. A. Englin, and T. Ya. Nikiforova, *Zh. Obshch. Khim.*, **38**, 709 (1968); (b) M. A. Englin, I. V. Ermakova, and V. I. Yakutin, *Ibid.*, **39**, 1134 (1969).
(4) M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, **48**, 4040 (1968).
(5) H. Hagemann, D. Arlt, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **8**, 606 (1969).
(6) V. A. Ginsburg and K. N. Smirnov, *Zh. Obsch. Khim.*, **37**, 1413 (1967); **39**, 1134, 1331 (1969).
(7) D. H. Dybrig, *Inorg. Chem.*, **5**, 1795 (1966).
(8) E. Kuchle, B. Anders, E. Klauke, H. Tarnow, and G. Zumach, *Angew. Chem., Int. Ed. Engl.*, **8**, 20 (1969).
(9) (a) M. S. Gordon and J. A. Pople, *J. Chem. Phys.*, **49**, 4643 (1968); (b) G. Ostorogovich, F. Kerek, and Z. Simon, *J. Chem. Soc. B*, 541 (1971).
(10) R. Ditchfield, J. E. Del Bene, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 703 (1972).
(11) For basis sets, see J. A. Pople, *Acc. Chem. Res.*, **3**, 217 (1970); W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). The program used with was GAUSSIAN-70, available as QCPE 236 from Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Ind.
(12) J. M. Howell and L. K. Kirshenbaum, *J. Am. Chem. Soc.*, preceding paper in this issue.
(13) L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 2371 (1972).
(14) L. C. Snyder and H. Basch, "Molecular Wave Functions and Properties", Wiley, New York, N.Y., 1972.
(15) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 2191 (1970).

Ionization Potentials of π Molecular Hydrocarbons[1a]

William C. Herndon*[1b]

Contribution from the Department of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968. *Received May 5, 1975*

Abstract: Adiabatic ionization potentials for cata- and peri-condensed benzenoid hydrocarbons, benzenoid systems with essential single bonds, nonalternant aromatic compounds, and open-chain and cyclic olefins are correlated with an empirical resonance theory that only requires enumeration of structures. For 29 compounds, the average deviation of calculated and experimental ionization potentials is ±0.16 eV and the correlation coefficient is 0.995. For 11 additional large aromatic hydrocarbons, not included in the original correlation, the deviation is ±0.08 eV. Predicted ionization potentials for several interesting nonbenzenoid compounds are listed.

A simple structure-resonance theory with a basis of Kekulé structures has been demonstrated to correlate and predict resonance energies,[2] heats of formation,[3] bond orders and bond lengths,[4] NMR coupling constants,[4] and several types of reactivity[5,6] with high precision. The resonance theory calculations require no more than an enumeration of structures[7] since it has also been shown that an algorithm, logarithm of the Kekulé corrected structure count (CSC),[6,8] gives an excellent approximation to the ground-state eigenvalue of the structure-function Hamiltonian matrix. The structures are enumerated by graph theoretical

---

* Address correspondence to the author at Chemistry Section, National Science Foundation, Washington, D.C. 20550.