

THEORETICAL STUDY OF KETENIMINE: GEOMETRY, ELECTRONIC PROPERTIES, FORCE CONSTANTS AND BARRIERS TO INVERSION AND ROTATION

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ABSTRACT

Non-empirical calculations of the structure and properties of ketenimine have been performed using nine Gaussian basis sets. Values for the bond lengths and angles, HOMO and LUMO energies, atomic charges, overlap populations, dipole moments, bond energies, force constants and barriers to nitrogen inversion and internal rotation are predicted.

INTRODUCTION

Ketenimines, as tautomers of aliphatic nitriles, are believed to participate as intermediates in a number of important chemical reactions. Stable ketenimines are attractive reagents in modern organic synthesis [1]. Therefore, we present here a theoretical study of ketenimine and some properties of this molecule as a necessary first step to the better understanding of its chemical reactivity.

COMPUTATIONAL DETAILS

Non-empirical calculations of the structure and properties of ketenimine were performed using nine Gaussian basis sets: STO-3G [2], 3-21G [3], 4-31G [4], 6-31G [5], DZ (4s2p/2s) [6], TZ (5s4p/3s) [7], 6-31**G [8], DZ + P (4s2p1d/2s1p) with exponents for Cd = 0.7327, Nd = 0.9084 and Hp = 0.90, and TZ + P (5s4p1d/3s1p) with the same exponents for the polarization functions. The correlation energy for ketenimine at the DZ level was calculated with the aid of the SCEP method [9]. The molecular geometry was optimized by the force gradient method with analytical gradients [10] as implemented in the MONSTERGAUSS 80 program [11]. SCEP [12] was modified and appended as a link to the IBM version of GAUSSIAN 76 [13].

RESULTS AND DISCUSSION

The geometry of ketenimine was optimized using five different basis sets. As Table 1 demonstrates, split-valence and double-zeta basis set calculations predict very similar bond lengths and angles. The C=C bond length is approximately the same as in allenes [14], and the C=N bond, as expected, is shorter than in, e.g. methylene imine [15], and closer in length to a triple bond. The minimal STO-3G basis calculations predict quite different bond lengths and angles involving the nitrogen atom from the rest of the data, due, almost certainly, to a worse representation of the lone electron pair. In general, predicted bond lengths and angles agree fairly well with the known X-ray data for triaryl ketenimines [16].

The calculated total energy of ketenimine, together with the HOMO and LUMO energies are presented in Table 2. One observes a lowering of HOMO and, to a larger extent, LUMO energies with the extension of the basis set. Addition of polarization functions to the 6-31G, DZ and TZ sets, however, does not change these orbital energies significantly. The contribution of single and double excitations to the ground-state energy of ketenimine is -0.2641 a.u., as given by the DZ-SCEP calculation with the three lowest molecular orbitals frozen to substitution.

Calculated atomic charges and overlap populations for the C=C and C=N bonds of ketenimine are given in Table 3. In general, extended basis sets predict stronger charge separation, but no regularity can be observed. The calculated dipole moments, given in the same Table, increase with extension of the basis set, but decrease with inclusion of polarization functions.

The calculated heat of atomization (STO-3G) of ketenimine (569 kcal

TABLE 1

Optimized molecular geometry of ketenimine. Bond lengths in Å, angles in degrees

Basis set	C1C2	C2N3	C1H4	N3H6	H4C1C2	H6N3C2
STO-3G ^a	1.292	1.242	1.079	1.047	121.1	111.6
3-21G	1.298	1.207	1.071	1.010	120.6	122.1
4-31G ^b	1.297	1.214	1.070	1.008	120.7	120.5
6-31G	1.304	1.217	1.076	1.002	120.6	122.5
DZ	1.314	1.225	1.071	1.005	120.5	122.2

^aSee also L. Ghosez and M. J. O'Donnell, in A. P. Marchand and R. E. Lehr (Eds.), *Pericyclic Reactions*, Academic Press, 1977, Vol. 2, p. 79; W. Runge, in S. Patai (Ed.), *The Chemistry of Ketenes, Allenes and Related Compounds*, Wiley-Interscience, 1980, Part 1, p. 45. ^bSee also A. C. Hopkinson, M. H. Lien, K. Yates, P. G. Mezey and I. G. Csizmadia, *J. Chem. Phys.*, 67 (1977) 517.



TABLE 2

Total, HOMO and LUMO energies of ketenimine (atomic units)

Basis set	Total energy	HOMO	LUMO
STO-3G	-130.1808	-0.2903	0.2861
3-21G	-131.1347	-0.3376	0.1765
4-31G	-131.6731	-0.3424	0.1663
6-31G	-131.8114	-0.3413	0.1616
DZ	-131.8145	-0.3469	0.1521
TZ/4-31G	-131.8475	-0.3489	0.1258
6-31**/4-31G	-131.8766	-0.3456	0.1693
DZ + P/4-31G	-131.8843	-0.3508	0.1619
TZ + P/4-31G	-131.9160	-0.3526	0.1287
DZ-SCEP/6-31G	-132.0786 ^a		

^aExpansion coefficient of the ground state in the correlated wavefunction, $C_0 = 0.897$. The three lowest SCF MO's are excluded from all SCEP calculations.

mol^{-1}) and the heat of formation (42 kcal mol^{-1}) are obtained via the following formula for bond energies [17]

$$E_{AB} = a_{AB}P_{AB}^3 + b_{AB}P_{AB}^2 + c_{AB}P_{AB}$$

where P_{AB} is the bond overlap population and a , b , c are empirical coefficients. The following values for bond energies were calculated: $E_{C-C} = 143$ (ethylene $E_{C-C} = 140$), $E_{C-N} = 135$ (methylene imine $E_{C-N} = 122$), $E_{CH} = 99$ and $E_{NH} = 93 \text{ kcal mol}^{-1}$.

The quadratic force constants of ketenimine [18] were calculated with the 6-31G basis set at the predicted equilibrium geometry. These force constants, listed in Table 4, predict (GF) a frequency of 2493 cm^{-1} for the asymmetric stretching mode $C=C=N$, which is 450 cm^{-1} higher than that assigned to ketenimine (2040 cm^{-1} [19]) and the observed frequencies of triaryl ketenimines [20]. This is a usual result for this type of calculation,

TABLE 3

Atomic charges, selected overlap populations and dipole moments of ketenimine

Basis set	C1	C2	N3	H4(5)	H6	C1C2	C2N3	μ (D)
STO-3G	-0.203	0.160	-0.310	0.084	0.183	0.612	0.555	1.67
3-21G	-0.424	0.429	-0.845	0.253	0.335	0.344	0.557	1.88
4-31G	-0.383	0.324	-0.702	0.207	0.348	0.564	0.554	2.11
6-31G	-0.428	0.303	-0.641	0.208	0.351	0.602	0.554	2.02
DZ	-0.562	0.181	-0.399	0.226	0.328	0.574	0.652	2.10
TZ/4-31G	-0.353	0.041	-0.391	0.201	0.301	0.559	0.657	2.12
6-31**/4-31G	-0.410	0.455	-0.689	0.167	0.310	0.636	0.624	1.73
DZ + P/4-31G	-0.447	0.228	-0.362	0.161	0.259	0.618	0.736	1.79
TZ + P/4-31G	-0.402	0.202	-0.390	0.166	0.258	0.609	0.724	1.82
DZ-SCEP/6-31G	-0.542	0.104	-0.292	0.216	0.301	—	—	—

TABLE 4

Calculated 6-31G harmonic force constants (uncorrected) for ketenimine, m dyn A^{-1} or mdyn A rad^{-1} . The definition of the internal coordinates is given below^a

1	2	3	4	5	6	7	8	9	10	11	12	13
12.446	-0.110	-0.110	-0.420	0.092	-0.400	-0.400	-0.391	0.140	-0.009	-0.009	0.005	-0.061
7.261	7.261	-0.027	0.040	0.002	-0.061	-0.061	0.051	-0.005	-0.003	-0.001	0.005	0.004
		7.261	0.040	0.002	0	0	0.051	-0.005	-0.001	-0.003	-0.005	0.004
			16.265	0.046	0	0	0.007	-0.900	-0.010	-0.010	0.007	0.102
				8.695	0.003	0.003	0	-0.369	-0.007	-0.007	0	0.041
					1.241	1.241	-0.800	0	0	0	0.073	-0.038
							-0.800	0	0	0	0.073	-0.038
							1.669	0	0.002	0.002	0	0
								0.814	-0.006	-0.006	-0.001	0.049
									0.299	0.243	-0.010	0.336
										0.299	-0.010	0.336
											0.534	0
												1.608



^aCoordinates 10, 11, 13 are out-of-plane bends.

TABLE 5

Barriers to nitrogen inversion and internal rotation of ketenimine (in kcal mol⁻¹)

Basis set	Inversion barrier	Rotation barrier
STO-3G	23.65	40.50
4-31G	9.22	26.72
DZ	7.65	26.22
TZ/4-31G	7.22	24.87
6-31**/4-31G	13.85	25.12
DZ + P/4-31G	12.59	24.56
TZ + P/4-31G	12.21	24.35
DZ-SCEP/4-31G	10.57	27.62

although frequencies within a few percent of the experimental values can be obtained by applying empirical corrections to the calculated harmonic force constants [21].

Ketenimines are axially dissymmetric, as are the analogous allenes. However, these molecules are configurationally unstable and the observed rapid inter-conversion of the two possible configurations [22] has been attributed to an inversion mechanism. Table 5 collects calculated energy barriers to nitrogen inversion and rotation around the C=C=N axis. These energies are obtained for reoptimized geometries and H6 fixed in the molecular plane (rotation) or along the extension of the C=N bond (inversion). All basis sets, except STO-3G, predict a relatively low inversion barrier, which corresponds well with the experimental NMR value of about 10 kcal mol⁻¹ [22]. Calculated rotation barriers are much higher, thus confirming the assignment of the configurational instability of ketenimines to nitrogen inversion.

Previous calculations on methylene imine [23] predict considerably higher barriers to inversion and rotation. As test calculations have shown, these results arise from neglect of molecular geometry changes during the simulated inversion or rotation. The error assumed in such cases may be larger than 300%.

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REFERENCES

- 1 M. W. Barker and W. E. McHenry, in S. Patai (Ed.), *The Chemistry of Ketenes, Allenes and Related Compounds*, Wiley-Interscience, 1980, Part 2, pp. 702-720; D. G. McCarthy and A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2*, (1980) 579.
- 2 W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.*, 51 (1969) 2657.
- 3 J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.*, 102 (1980) 939.
- 4 R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 54 (1971) 724.

- 5 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 56 (1972) 2257.
- 6 L. C. Snyder and H. Basch, *Molecular Wave Functions and Properties*, Wiley-Interscience, 1972, pp. 22-25.
- 7 T. H. Dunning, *J. Chem. Phys.*, 55 (1971) 716.
- 8 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 28 (1973) 213.
- 9 W. Meyer, *J. Chem. Phys.*, 64 (1976) 2901; C. Dykstra, H. F. Schaefer III and W. Meyer, *J. Chem. Phys.*, 65 (1976) 2740.
- 10 H. B. Schlegel, Ph. D. Thesis, Queen's University, Kingston, Ontario, Canada.
- 11 M. Peterson and R. Poirier, University of Toronto, Toronto, Ontario, Canada; W. C. Davidson and L. Nazareth, Argonne Natl. Lab. Tech. Memos 303 and 306, Argonne, Illinois, U.S.A.
- 12 C. E. Dykstra, *QCPE*, 11 (1979) 246.
- 13 C. M. Cook, *QCPE*, 12 (1980) 391.
- 14 C. E. Dykstra and H. F. Schaefer III, in S. Patai (Ed.), *The Chemistry of Ketenes, Allenes and Related Compounds*, Wiley-Interscience, 1980, Part 1, pp. 1-44.
- 15 J. M. Howell, *J. Am. Chem. Soc.*, 98 (1976) 886; P. Botschwina, *Chem. Phys. Lett.*, 29 (1974) 580.
- 16 R. R. Naqva and P. J. Wheatley, *J. Chem. Soc. A*, (1970) 2053.
- 17 G. Leroy, M. T. Nguyen and M. Sana, *Tetrahedron*, 34 (1978) 2459.
- 18 H. B. Schlegel, S. Wolfe and F. Bernardi, *J. Chem. Phys.*, 67 (1977) 4181.
- 19 M. E. Jacox, *Chem. Phys.*, 43 (1979) 157.
- 20 S. Stankovsky and S. Kovac, *Chem. Zvesti*, 28 (1974) 234.
- 21 P. Pulay and W. Meyer, *Mol. Phys.*, 27 (1974) 473; W. Meyer and P. Pulay, *Theor. Chim. Acta*, 32 (1974) 253; Y. Sugawara, Y. Hamada, A. Hirakawa, M. Tsuboi, S. Kato and K. Morokuma, *Chem. Phys.*, 50 (1980) 105.
- 22 J. C. Jochims, S. Herzberger, B. Gambke and F. A. K. Anet, *Tetrahedron Lett.*, (1977) 2255.
- 23 R. Macaulay, L. A. Burnelle and C. Sandorfy, *Theor. Chim. Acta*, 29 (1973) 1; G. Leroy, M. T. Nguyen, M. Sana and J.-L. Villaveces, *Bull. Soc. Chim. Belg.*, 89 (1980) 1023.