Weakly Bound Complexes of N_2O: An ab Initio Theoretical Analysis Toward the Design of N_2O Receptors

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Ab initio calculations at MP2/6-311++G(2d,2p) and MP2/6-311++G(3df,3pd) computational levels have been used to analyze the interactions between nitrous oxide and a series of small and large molecules that act simultaneously as hydrogen bond donors and electron donors. The basis set superposition error (BSSE) and zero point energy (ZPE) corrected binding energies of small N_2O complexes (H_2O, NH_3, HOOH, $HOO^\bullet$, $HONH_2$, HCO_2H, H_2CO, $HCONH_2$, H_2CNH, $HC(NH)NH_2$, SH_2, H_2CS, HCSOH, $HCSNH_2$) vary between −0.93 and −2.90 kcal/mol at MP2/6-311++G(3df,3pd) level, and for eight large complexes of N_2O they vary between −2.98 and −3.37 kcal/mol at the MP2/6-311++G(2d,2p) level. The most strongly bound among small N_2O complexes ($HCSNH_2-N_2O$) contains a NH••N bond, along with S → N interactions, and the most unstable (H_2S-N_2O) contains just S → N interactions. The electron density properties have been analyzed within the atoms in molecules (AIM) methodology. Results of the present study open a window into the nature of the interactions between N_2O with other molecular moieties and open the possibility to design N_2O abiotic receptors.

Introduction

Nitrous oxide or laughing gas (N_2O) is a colorless nonflammable gas that is used in surgery and dentistry for its anaesthetic and analgesic effect.[1] It is also used as an oxidizer in internal combustion engines. In the atmosphere, nitrous oxide acts as greenhouse gas.

Recently, the study of weakly bound van der Waals N_2O complexes has attracted a lot of interest. Using high-resolution infrared spectroscopy combined with molecular beam techniques, detailed information on the structure was obtained. The goal was accurate descriptions of the intermolecular interactions which can lead, in general, to an improved understanding of intermolecular potentials. The structures of a series of mixed N_2O van der Waals clusters, that is, $Ar-N_2O$,[2−4] N_2-N_2O,[5] $CO-N_2O$,[6] $HF-N_2O$,[7] $HCl-N_2O$,[8] $HBr-N_2O$,[7] $HCN-N_2O$,[9] N_2O-N_2O,[10] CO_2-N_2O,[11] H_2O-N_2O,[12] $HCCH-N_2O$,[13] $(N_2O)_3$,[14] and the open-shell complex O_2-N_2O,[14,15] have been determined from their rotational constants. To our best knowledge, results of theoretical studies concerning weakly bound complexes of N_2O are rare, and we just found theoretical studies of N_2O-N_2O,[16] SO_2-N_2O,[16] $(SO_2)_2-N_2O$,[15,16] $(Rg)_2-N_2O$,[17] and $(N_2O)_3$[14] complexes in literature.

We have, initially, studied the complexes formed between N_2O and small systems that act as HB donors and electron donors simultaneously. So far, there is no theoretical or experimental data available concerning interaction of N_2O with the molecules studied in the present study (except N_2O-H_2O). From the information obtained with the mentioned complexes, larger molecules have been considered where three simultaneous interactions can occur with N_2O. These new molecules can be considered as simplified models for N_2O receptors. In the absence of experimental information about the structures or energetics of the studied complexes, a theoretical analysis of their properties appear to be in order. The present work thus reports, for the first time, a detailed examination of the stabilities and electronic structure of the studied complexes.

Computational Details

Calculations were performed using the Gaussian03 program.[18] Geometry optimizations and frequency calculations were performed at the MP2 level[19] using the 6-311++G(2d,2p) and 6-311++G(3df,3pd) basis sets.[20] MP2 calculations with triple-Z basis sets have proved to provide very good results when compared to experimental data of weakly bonded complexes.[21,22]

Harmonic vibrational frequency calculations were performed to confirm that the obtained structures were local minima in the potential energy surfaces (PESs) of the studied complexes. The counterpoise (CP) method[23] was used to correct the basis set superposition error (BSSE) in the calculation of the binding energy.

The electron density of the monomers and complexes has been analyzed at the MP2/6-311++G(2d,2p) computational level within the atoms in molecules methodology[24] (AIM) with the AIMPAC and MORPHY98 programs.[25,26] The atomic integration within the atomic basins has been to obtain the atomic contribution to the total energy, charge, and volume of the systems. The quality of the integration has been assessed on the basis of the value of the integrated Laplacian for each individual atom. It has been shown that integrated Laplacian values smaller than 1×10^{-3} provide very small error when comparing the sum of the integrated values versus the corresponding sum obtained directly from the ab initio calculation.[27] In the present case, the larger error in the total energy has been 0.16 kcal/mol.

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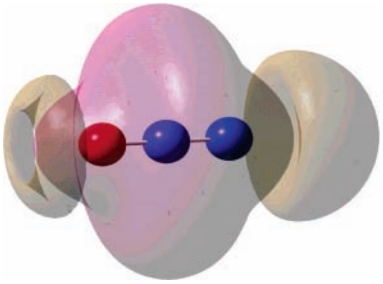


Figure 1. Molecular electrostatic potential of ONN at the MP2/6-311++G(2d,2p) level. The isosurfaces represented are ± 0.01 au.

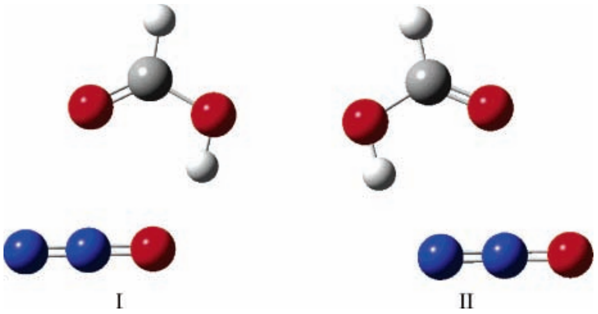


Figure 2. Optimized geometry at the MP2/6-311++G(2d,2p) computational level of the two complexes of N_2O:HCOOH.

TABLE 1: Energetic of the Small Complexes of N_2O (kcal/mol) Studied at the MP2/6-311++G(2d,2p) and MP2/6-311++G(3df, 3pd) Computational Levels[a]

	MP2/6-311++G (2d, 2p)			MP2/6-311++G (3d f,3pd)		
	EI	EI + BSSE	EI + BSSE + ZPE	EI	EI + BSSE	EI + BSSE + ZPE
H_2O	−2.53	−2.03	−1.32	−2.64	−2.23	−1.48
NH_3	−2.48	−1.97	−1.35	−2.59	−2.20	−1.62
HOOH (I)	−3.43	−2.51	−1.69	−3.72	−2.79	−1.92
HOOH (II)	−3.39	−2.58	−1.74	−3.78	−2.90	−1.99
HOO (I)	−3.96	−2.96	−1.90	−4.35	−3.35	−2.18
HOO (II)	−3.82	−2.96	−1.84	−4.31	−3.39	−2.16
$HONH_2$ (I)	−3.64	−2.79	−1.96	−3.92	−3.09	−2.23
$HONH_2$ (II)	−3.59	−2.84	−1.96	−3.98	−3.19	−2.28
HCOOH (I)	−4.18	−3.06	−2.31	−4.44	−3.47	−2.69
HCOOH (II)	−4.00	−3.06	−2.25	−4.32	−3.34	−2.51
H_2CO (I)	−2.56	−1.91	−1.29	−2.77	−2.22	−1.56
H_2CO (II)	−2.71	−2.10	−1.41	−2.98	−2.43	−1.70
$HCONH_2$ (I)	−4.00	−3.08	−2.44	−4.27	−3.47	−2.73
$HCONH_2$ (II)	−3.95	−3.17	−2.61	−4.33	−3.63	−2.80
H_2CNH (I)	−3.23	−2.58	−1.98	−3.52	−2.91	−2.21
H_2CNH (II)	−3.31	−2.70	−2.04	−3.66	−3.05	−2.30
$HC(NH)NH_2$ (I)	−4.43	−3.49	−2.85	−4.74	−3.90	−3.23
$HC(NH)NH_2$ (II)	−4.36	−3.55	−2.85	−4.78	−4.00	−3.25
SH_2	−1.73	−1.17	−0.65	−1.95	−1.45	−0.93
H_2CS (I)	−2.42	−1.70	−1.17	−2.73	−2.11	−1.54
H_2CS (II)	−2.68	−2.03	−1.45	−3.08	−2.45	−1.81
HCSOH (I)	−4.07	−2.86	−2.20	−4.50	−3.38	−2.62
HCSOH (II)	−3.97	−2.92	−2.19	−4.44	−3.47	−2.71
$HCSNH_2$ (I)	−3.91	−2.90	−2.32	−4.32	−3.38	−2.72
$HCSNH_2$ (II)	−3.97	−3.10	−2.41	−4.48	−3.65	−2.90

[a] (I) and (II) indicate that the HB is formed with the O and N_t of N_2O, respectively.

TABLE 2: Correlation Between the Energetic Results Obtained at the MP2/6-311++G(3df,3pd) and MP2/6-311++G(2d,2p) Levels in Present Study

	EI	EI + BSSE	EI + BSSE + ZPE
R^2	0.9886	0.9849	0.9799
slope	1.09	1.09	1.06
intercept	−0.03	−0.15	−0.20

TABLE 3: Selected Geometries of the Complexes (*R*, in Å) Studied at the MP2/6-311++G(2d,2p) and MP2/6-311++G(3df,3pd) Computational Levels

	MP2/6-311++G (2d,2p)			MP2/6-311++G (3df,3pd)		
	$R_{O(N\ or\ S)\rightarrow Ni}$[a]	$R_{H...Nt}$	$R_{H...O}$	$R_{O(N\ or\ S)\rightarrow Ni}$	$R_{H...Nt}$	$R_{H...O}$
H_2O	2.851			2.809		
NH_3	3.046			3.013		
HOOH (I)[b]	2.939		2.155	2.888		2.141
HOOH (II)	2.946	2.205		2.895	2.184	
HOO (I)	2.997		2.042	2.923		2.020
HOO (II)	3.096	2.073		2.966	2.056	
$HONH_2$ (I)	3.033		2.201	2.988		2.181
$HONH_2$ (II)	3.023	2.241		2.982	2.223	
HCOOH (I)	2.949		2.051	2.901		2.036
HCOOH (II)	2.989	2.118		2.932	2.108	
H_2CO (I)	2.932		2.713	2.881		2.669
H_2CO (II)	2.927	2.720		2.879	2.682	
$HCONH_2$ (I)	2.921		2.267	2.875		2.260
$HCONH_2$ (II)	2.931	2.342		2.883	2.328	
H_2CNH (I)	2.977		2.737	2.923		2.689
H_2CNH (II)	2.967	2.736		2.923	2.698	
$HC(NH)NH_2$ (I)	2.986		2.276	2.945		2.264
$HC(NH)NH_2$ (II)	2.975	2.364		2.934	2.340	
SH_2	3.455			3.351		
H_2CS (I)	3.488		2.588	3.395		2.555
H_2CS (II)	3.461	2.597		3.374	2.564	
HCSOH (I)	3.472		2.008	3.378		1.991
HCSOH (II)	3.507	2.061		3.387	2.059	
$HCSNH_2$ (I)	3.494		2.172	3.392		2.169
$HCSNH_2$ (II)	3.485	2.230		3.376	2.242	

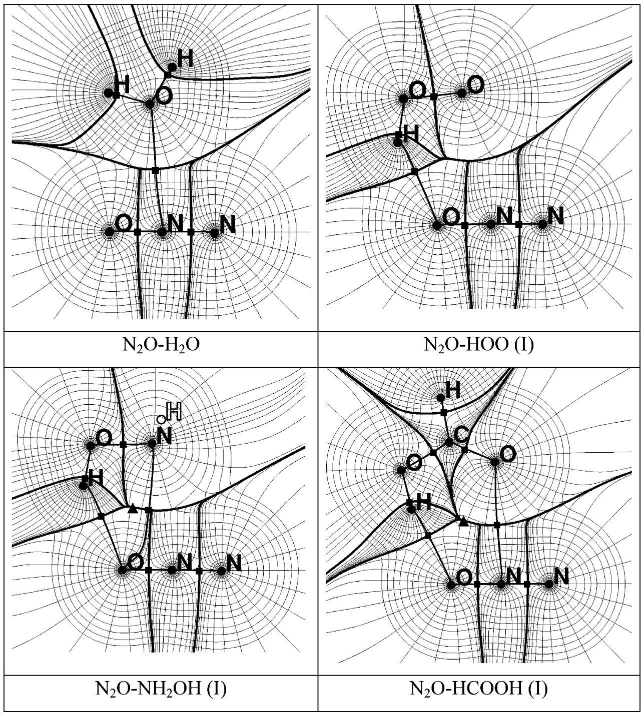
[a] Subscripts i and t stand for interior nitrogen atom and terminal nitrogen atom, respectively. [b] (I) and (II) indicate that the HB is formed with the O atom and N_t of N_2O, respectively.

Results and Discussion

Complexes with Small Molecules. The geometrical and electronic characteristic of the isolated N_2O molecule are nicely reproduced by the calculations. Thus, the calculated NN and NO bond distances are 1.157/1.154 Å and 1.185/1.178 Å for the MP2/6-311++G(2d,2p) and MP2/6-311++G(3df,3pd) computational levels and 1.128 and 1.184 Å experimentally.[28] In the same way, the calculated dipole moment, 0.167/0.179 debyes, is close to the experimental one (0.142 debyes).[29]

The literature results of the N_2O−HF complexes show the existence of two minima with the HF molecule forming a hydrogen bond (HB) with both ends of the N_2O molecule.[30] However, the interaction of N_2O with HCl shows an additional minimum where the central nitrogen of N_2O interacts with the chlorine atom.[31] This complex is the most stable one in agreement with the experimental data. In the case of the N_2O−H_2O complex, two minima complexes have been found. The most stable one corresponds to that where an electron donor−acceptor interaction is established. The other one presents a HB with the nitrogen atoms of N_2O and a BSSE and zero point energy (ZPE) corrected interaction energy of −0.57 kcal/mol at the MP2/6-311++G(2d,2p) computational level. The latter complex will not be considered further in this article (the Cartesian coordinates of the optimized complex are available in the Supporting Information).

These results are in agreement with the molecular electrostatic potential of N_2O that presents a large and positive region around the inner N atom, N_i, and two negative regions in the terminal N and O atoms (Figure 1). In the present case, for the simplest molecules, H_2O, NH_3, and SH_2, only the possibility of an electron donor−acceptor complex has been considered. For the rest of the cases where a fragment of the molecule can be involved in the donor−acceptor interaction and another fragment can form a HB with N_2O, two different configurations have been considered: the first one with the HB with the terminal oxygen atom and the second one with the terminal nitrogen (N_t). These structures were calculated to be minima at MP2/6-311++G(2d,2p) and MP2/6-311++G(3df,3pd) computational levels (Figure 2 shows the two complexes of N_2O:HCOOH).



N_2O-H_2O N_2O-HOO (I)

N_2O-NH_2OH (I) N_2O-HCOOH (I)

Figure 3. An example of the four-electron density topologies found in the complexes studied. The bcp's are represented with squares, the rcp's with triangles, and the positions of the atoms with circles.

TABLE 4: Contributions to E_I and $E_{I+BSSE+ZPE}$ [MP2/6-311++G(2d,2p)] in kcal/mol

	E_I	$E_{I+BSSE+ZPE}$
ring (HB)	−1.11	−0.90
O···N	−2.97	−1.52
N···N	−3.39	−1.97
S···N	−2.76	−1.36
radical	−0.92	−0.35
points	22	22
R^2	0.997	0.997
SD	0.24	0.13

The computed binding energies of the small complexes studied are reported in Table 1. The correlation between the results of the two basis sets indicates that both levels provide similar information, however, the MP2/6-311++G(3df,3pd) results are always slightly larger, in absolute value, than the MP2/6-311++G(2d,2p) ones (Table 2). The computed binding energies vary between −1.45 and −3.65 kcal/mol for the H_2S−N_2O and $HCSNH_2$−N_2O complexes, respectively, at MP2/6-311++G(3df,3pd) level.

The most important intermolecular distances found in the complexes considered are gathered in Table 3. The calculated interatomic distance of the N_2O−H_2O complex is slightly shorter that the experimental one (2.97 Å)[12] probably because of not considering the vibrational effect in the calculations. The interatomic distances obtained with the MP2/6-311++G(2d,2p) level are longer than the corresponding ones obtained at the MP2/6-311++G(3df,3pd), except for the hydrogen bond formed in the complex **I** of $HCSNH_2$. These results are in agreement with the energetic tendency that shows larger interaction energy with the last computational level.

The comparison of complex **I** and **II** of each molecule shows larger interaction energies for complex **I** than for complex **II** and, correspondingly, the H···O distances are shorter than H···N_t ones.

If the total interaction energy of the complexes can be considered as the sum of the electron donor−electron acceptor interaction and the hydrogen bond, and the complexes with H_2O, NH_3 and SH_2 are used as models, it is obvious that the stronger interaction corresponds to the electron donor−acceptor interaction for the two first cases and to the hydrogen bond to those cases where the sulfur atom acts as an electron donor. In addition, the geometrical disposition of the electron donor and the HB donor groups seems to be important. Thus, the interaction is larger for those cases where the two groups are separated by two bonds as in HCOOH, $HCONH_2$, and their sulfur derivatives versus those cases where the separation is only one bond as in HOOH and NH_2OH.

The role of the dispersion forces in these complexes has been evaluated by calculating the complexes at the HF/6-311++G(3df,3pd) computational level. While the results are similar to those obtained in configuration **I** at MP2 level, the ones of configuration **II** present a reinforcement of the HB and the absence of the interaction with the central nitrogen atom of N_2O.

The electron density of the complexes has been analyzed with the atoms in molecules methodology (AIM). Several different topologies of this property have been found in the studied

TABLE 5: Electron Density Properties (au) at the Intermolecular bcp

	O(N,S)→Ni		O(N,S)→O		H···O		H···Nt	
	Rho	Lap	Rho	Lap	Rho	Lap	Rho	Lap
H_2O	0.0088	0.0416						
NH_3	0.0082	0.0314						
HOOH (I)			0.0086	0.0350	0.0144	0.0555		
HOOH (II)	0.0092	0.0353					0.0140	0.0523
HOO (I)					0.0186	0.0705		
HOO (II)							0.0189	0.0677
$HONH_2$ (I)			0.0088	0.0326	0.0130	0.0507		
$HONH_2$ (II)	0.0096	0.0335					0.0129	0.0490
HCOOH (I)	0.0081	0.0341			0.0173	0.0638		
HCOOH (II)	0.0092	0.0353					0.0163	0.0575
H_2CO (I)	0.0085	0.0357			0.0060	0.0240		
H_2CO (II)	0.0089	0.0351					0.0062	0.0233
$HCONH_2$ (I)	0.0086	0.0353			0.0114	0.0434		
$HCONH_2$ (II)	0.0085	0.0339					0.0106	0.0396
H_2CNH (I)	0.0089	0.0360			0.0056	0.0229		
H_2CNH (II)	0.0094	0.0355					0.0059	0.0224
$HC(NH)NH_2$ (I)	0.0090	0.0344			0.0110	0.0417		
$HC(NH)NH_2$ (II)	0.0093	0.0351					0.0100	0.0368
SH_2	0.0056	0.0220						
H_2CS (I)			0.0058	0.0213	0.0069	0.0255		
H_2CS (II)	0.0063	0.0215					0.0073	0.0264
HCSOH (I)	0.0059	0.0214			0.0187	0.0685		
HCSOH (II)	0.0063	0.0202					0.0184	0.0631
$HCSNH_2$ (I)	0.0059	0.0198			0.0134	0.0508		
$HCSNH_2$ (II)	0.0060	0.0199					0.0130	0.0476

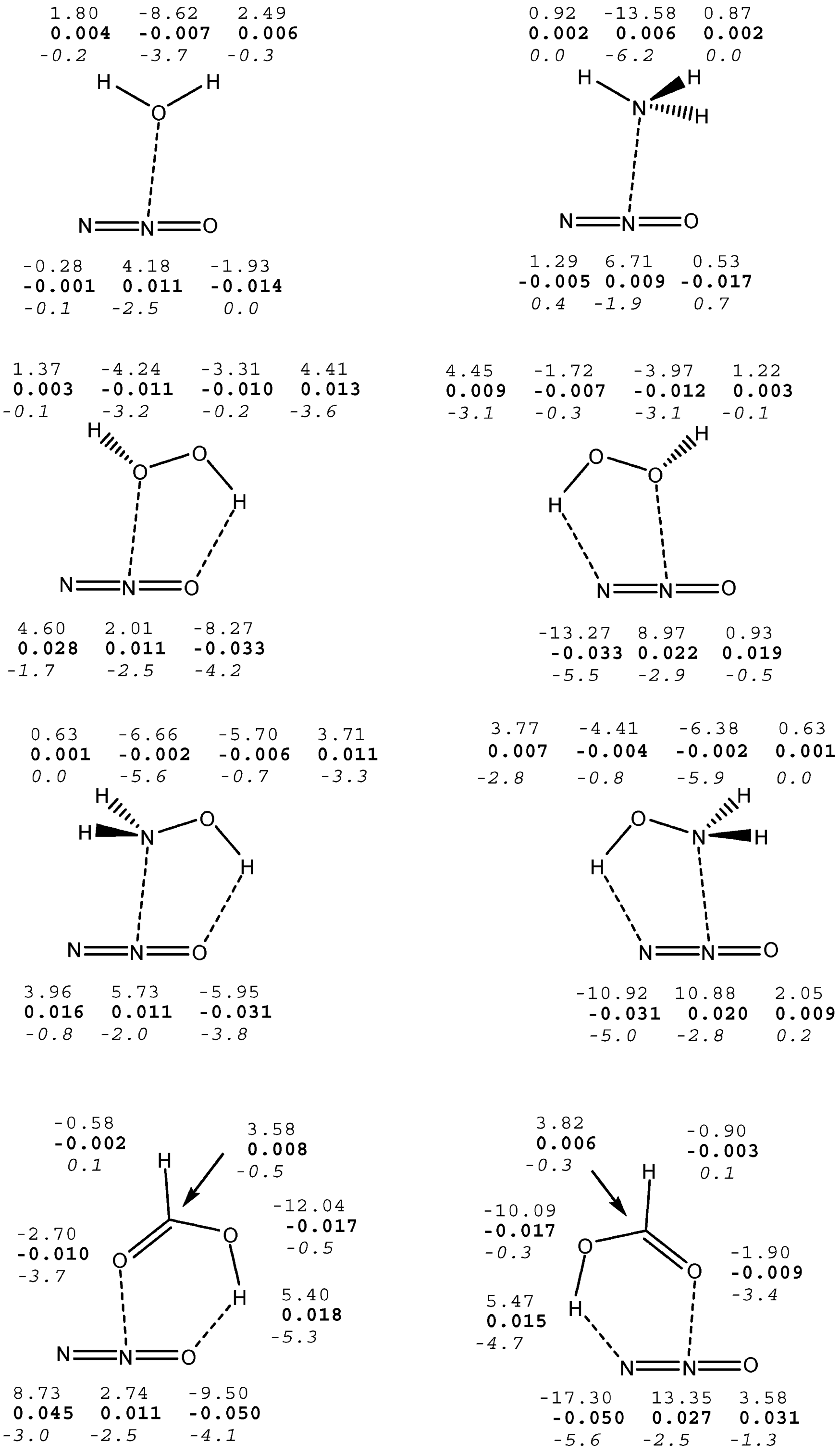


Figure 4. Atomic variation of the energy, charge (in bold), and volume (in italic), in atomic units, upon complex formation.

complexes (Figure 3). Three of the complexes (N_2O-OH_2, N_2O-NH_3, and N_2O-SH_2) present a unique intermolecular bond critical point between the central nitrogen atom of N_2O and the electron donor atom of the other molecule. The two complexes of the radical HOO present a unique bond critical point (bcp) between the hydrogen atom and the corresponding HB acceptor of N_2O. The complexes of NH_2OH and HOOH in configuration **I** present the bond critical point of the HB formation and an additional bcp between the second electron donor atom and the oxygen of N_2O. Finally, the rest of the complexes present two bcp's which correspond to a HB and an electron donor−electron acceptor interaction with the central nitrogen of N_2O. In addition, a ring critical point (rcp) is found in those cases where two intermolecular bcp's are present.

The presence of bcp between two nonbonded oxygen atoms[32,33] or two electronegative atoms[34,35] has been already described in other complexes and has been used to explain, in some cases, the relative stabilization of the corresponding species versus other configurations where it does not exist.

The values of the electron density and the Laplacian of the bcp are gathered in Table 5. In all the cases, the interactions correspond to closed-shell interactions as indicated by the positive value of the Laplacian. A more detailed analysis of

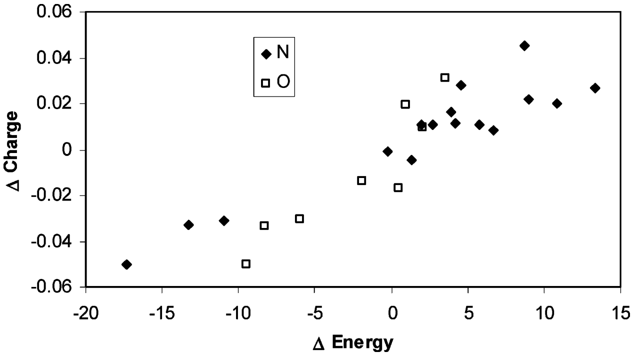


Figure 5. Atomic variation of the energy (kcal/mol) versus the charge variation (e) for the atoms of N_2O upon the dimer formation.

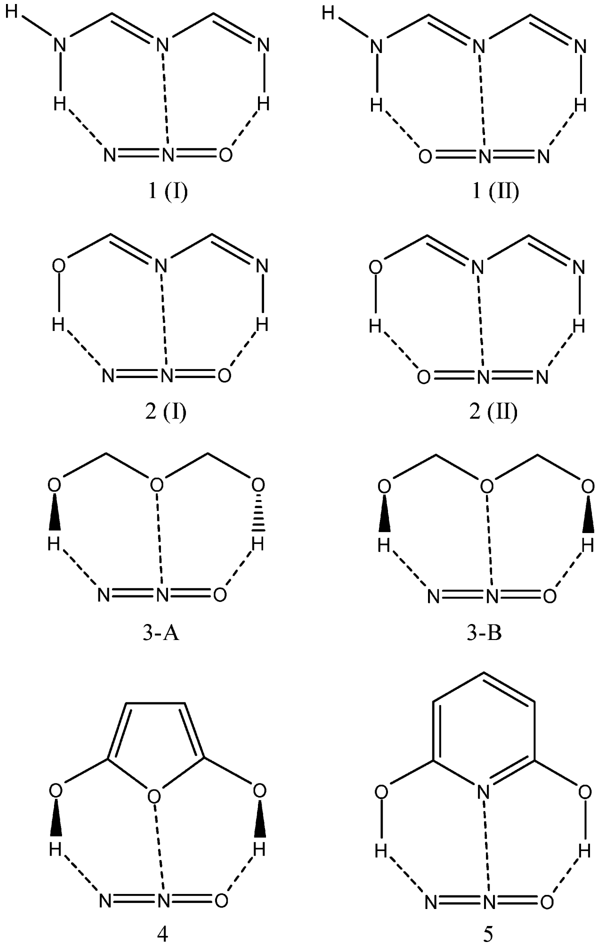

1 (I) 1 (II)
2 (I) 2 (II)
3-A 3-B
4 5

Figure 6. Schematic representation of the complexes of N_2O with models of N_2O receptor.

TABLE 6: Energetics (kcal/mol) of the Complexes Shown in Figure 6 at the MP2/6-311++G(2d,2p) Computational Level

complex	EI	EI + BSSE	EI + BSSE + ZPE
1 (I)	−5.17	−4.03	−3.37
1 (II)	−5.05	−3.86	−3.25
2 (I)	−5.27	−3.93	−3.22
2 (II)	−5.20	−3.94	−3.18
3-A	−4.99	−3.61	−3.00
3-B	−5.40	−3.81	−2.98
4	−5.49	−3.64	−3.03
5	−5.50	−3.98	−3.32

the values will be carried out after the study of the models of N_2O receptors.

TABLE 7: Selected Geometries (Å) of the Complexes Shown in Figure 6 Calculated at the MP2/6-311++G(2d,2p) Computational Level

complex	$R_{O(N)\to Ni}$[a]	$R_{H...Nt}$	$R_{H...O}$
1 (I)	2.968	2.334	2.582
1 (II)	2.982	2.680	2.256
2 (I)	2.972	2.780	2.054
2 (II)	2.967	2.124	2.704
3-A	2.850	3.031	2.258
3-B	2.897	2.334	2.277
4	2.855	2.505	2.348
5	2.974	2.263	2.163

[a] Subscripts i and t stand for interior nitrogen atom and terminal nitrogen atom, respectively.

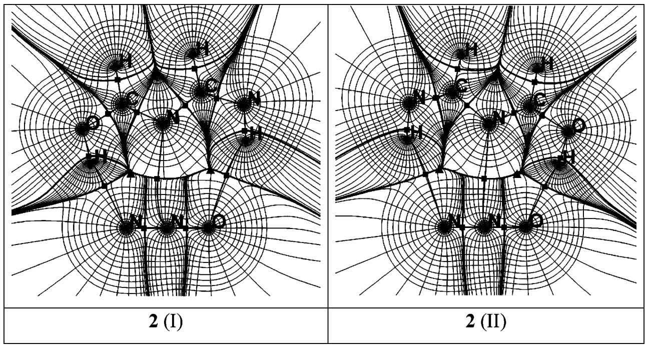

2 (I) **2** (II)

Figure 7. Electron density topologies of **2**(I) and **2**(II). The bcp's are represented with squares, the rcp's with triangles, and the positions of the atoms with circles.

TABLE 8: Electron Density Properties (au) at the Intermolecular bcp of the Complexes Shown in Figure 6

	O(N)→Ni		H···Nt		H···O	
complex	Rho	Lap	Rho	Lap	Rho	Lap
1 (I)	0.0096	0.0358	0.0106	0.0393	0.0063	0.0214
1 (II)	0.0093	0.0349	0.0056	0.0185	0.0114	0.0435
2 (I)	0.0094	0.0361	0.0046	0.0152	0.0170	0.0626
2 (II)	0.0099	0.0358	0.0160	0.0560	0.0049	0.0168
3-A	0.0096	0.0419	0.0042	0.0161	0.0118	0.0436
3-B	0.0098	0.0396	0.0107	0.0396	0.0110	0.0415
4	0.0101	0.0426	0.0081	0.0306	0.0099	0.0372
5	0.0098	0.0359	0.0115	0.0417	0.0132	0.0492

The integration of the electron density within the atomic basins has provided the atomic contribution to the total energy, charge, and volume. The comparison of the results obtained for the monomers and the complexes provides a tool to analyze the flow of energy and charge because of the interaction (Figure 4).

All the hydrogen atoms involved in the HB lost energy and became more positively charged, and their volume decreased in agreement with the proposed electron density criteria of Koch and Popelier for the detection of HB interactions.[36] The variation of these properties is similar for the two configurations (**I** and **II**) in each of the three pairs of complexes considered.

In the hydrogen-bonded complexes, the atom of N_2O that acts as HB acceptor is energetically stabilized and gains electron density while the other two are destabilized and lose charge. In concordance with a previous report that shows a relationship between the energetic and charge variation,[37] a similar finding has been obtained here (Figure 5).

The variations in the atoms of the molecules that interact with N_2O always tend to energetically stabilize and gain charge with the more electronegative atoms, N and O, while the hydrogen atoms are destabilized and become more positively charged.

In all the complexes considered, there is a volume reduction with respect to the sum of the volumes of the monomers as an indication of an electronic overlap. The maximum value corresponds to the $N_2O{-}HCO_2H$ complex in configuration **I**, where the reduction is 19.5 au which corresponds to 2.8% of the total volume of this system.

Models of N_2O Receptors. On the basis of the results obtained for the complexes of N_2O with small molecules, it has been considered interesting to explore the possibility of larger systems that could present three simultaneous interactions with N_2O and, at the same time, provide a basis for the development of N_2O receptors. The importance of nitrous oxide to life sciences mediated through the $GABA_A$ and NMDA receptors cannot be stressed too much.[38−40] Paradoxically, there is very little information about interactions between N_2O and abiotic molecules. A search in the Cambridge Structural Database[41] produces only one hit, EMECH. This inclusion crystal, $\{[Rh(II)_2(bza)4(pyz)]_n \cdot 3n(N_2O)\}$, was characterized by single-crystal X-ray diffraction analysis showing linear alignment of nitrous oxide molecules, $(N_2O)_n$, coherently generating channels of host rhodium benzoate pyrazine complexes.[42] Decamethylcucurbit[5]uril absorbs and releases N_2O more efficiently than other gases such as N_2, NO, and CO_2.[43] Finally, it is known that zeolites absorb N_2O and that this has important consequences for catalytic processes.[44,45]

The complexes studied are shown in Figure 6. The calculations level applied for these complexes has been the MP2/6-311++G(2d,2p) one since it provides similar results to the ones obtained with the larger basis set for a lesser computational cost.

The interaction energies of the complexes studied are gathered in Table 6. In all the cases, the interaction energies are larger, in absolute value, than the ones obtained in the complexes with the small molecules. The minimum and maximum values of the BSSE and ZPE corrected interaction energies are −2.98 and −3.37 kcal/mol for the **3**-B and **1**(I) complexes, respectively.

The interatomic distances obtained for the optimized structures are shown in Table 7. In general, the values obtained for these complexes are similar to the ones described previously.

The electron density of all the complexes studied in this section presents three intermolecular bcp's because of the two HBs and the electron donor−acceptor interaction as shown in Figure 7 for the two configurations of **2**. In addition, two rcp's are obtained. The values of the electron density and Laplacian at the bcp are gathered in Table 8. As previously, in all cases positive Laplacians are obtained and small values of the electron density are also obtained.

Using all the values of the bcp in the HB reported in the present article (Tables 5 and 8), exponential relationships have been found for the electron density and the Laplacian for the H⋯N and H⋯O hydrogen bonds formed versus the interatomic distance (eqs 1−4). Similar relationships have been described for other HB in the literature as an indication of the generality of this relationship.[46−48]

$$\mathrm{Rho}(\mathrm{O}\cdots\mathrm{H}) = 0.5837 \times \exp[-1.7279 \times (\mathrm{O}\cdots\mathrm{H\ distance})] \quad R^2 = 0.98,\ n = 19 \quad (1)$$

$$\mathrm{Lap}(\mathrm{O}\cdots\mathrm{H}) = 2.1907 \times \exp[-1.7282 \times (\mathrm{O}\cdots\mathrm{H\ distance})] \quad R^2 = 0.96,\ n = 19 \quad (2)$$

$$\mathrm{Rho}\ (\mathrm{N}\cdots\mathrm{H}) = 0.5184 \times \exp[-1.6483 \times (\mathrm{N}\cdots\mathrm{H\ distance})] \quad R^2 = 0.97,\ n = 19 \quad (3)$$

$$\mathrm{Lap}\ (\mathrm{N}\cdots\mathrm{H}) = 1.7941 \times \exp[-1.6283 \times (\mathrm{N}\cdots\mathrm{H\ distance})] \quad R^2 = 0.95,\ n = 19 \quad (4)$$

Conclusion

A theoretical study of the simultaneous HB and electron donor−acceptor interactions in complexes with N_2O has been carried out at the MP2/6-311++G(2d,2p) and MP2/6-311++G(3df,3pd) computational levels. The results indicate that the N_2O molecule can form up to three interactions and thus models of N_2O receptors have been proposed on the basis of this observation.

The electron density of the complexes has been analyzed and different topologies have been found. The energy, charge, and volume atomic partition within the AIM methodology has allowed the analyzation of the effect of complexation in these properties.

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Supporting Information Available: Cartesian coordinates of the optimized complexes at the MP2/6-311++G(2d,2p) computational level. This material is available free of charge via the Internet at http://pubs.acs.org.

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