Molecular Orbital Studies of Molecular Exciplexes. Part 1: AM1 and PM3 Calculations of the Ammonia–Oxygen Complex and its Solvation by Water

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Ground- and excited-state calculations of the triplet $O_2 \cdot NH_3 \cdot nH_2O$ complex as a model for solution photo-oxygenation of amines by triplet oxygen are reported at the AM1 and PM3 SCF–MO levels. For $n < 3$, the first excited AM1 triplet state corresponds to local excitation on the ammonia (T_N), whereas the polar excited state (T_P) corresponding to $NH_3^{+} \cdot O_2^{-} \cdot$ becomes the lowest excited triplet state when $n \geq 3$. In contrast, the lowest excited PM3 triplet state is ionic even for $n = 0$, and the T_P and ground-state (T_0) triplet surfaces intersect at an N–O distance of 1.95 Å for $n = 5$, with T_P becoming a local minimum on ground triplet state surface at shorter N–O distances. The reliability of these models are discussed in terms of known errors and properties of the AM1 and PM3 methods, and by a comparison of the solvation enthalpies and structures of systems such as $NH_4^{+} \cdot nH_2O$, $NH_4^{+} \cdot nNH_3$, and $HO^{-} \cdot nH_2O$ ($n = 1$–4) with known experimental values.

Light-induced oxygenation of organic compounds has long been the subject of extensive investigation. Singlet oxygen [1] is generally assumed to be the reactive species in the majority of photo-oxygenation reactions involving molecular oxygen, but there are a number of reactions [2] where oxygenation proceeds under conditions where no singlet oxygen can be formed. One common example is the formation of hydroperoxides in rubber and similar materials exposed to the air and sun, and many so called 'auto-oxidation processes' may also belong to this category. We have investigated experimentally one such reaction,[3] for which the mechanism is thought to involve the formation of a loose complex between triplet oxygen and the substrate.[4] The absorption of light causes the formation of a charge-transfer complex, which can then undergo chemical transformation to the products (Scheme).

$$\underset{T_0}{A + O_2} \xrightarrow{h\nu} \underset{T_P}{[A^{\cdot +} + O_2^{\cdot -}]} \longrightarrow \text{Products}$$

Scheme.

Measurement of the rate constants involved in such reactions can be difficult experimentally.[3] For this reason we wished to investigate various theoretical procedures for modelling photo-oxygenation and for predicting specific substituent and structural effects on the course of the reaction. The involvement of ionic excited state intermediates also renders the reaction sensitive to interactions with *e.g.* polar solvents such as water. These properties, together with a requirement to handle relatively large substituents such as phenyl or similar stabilising groups, and the need for effective geometry optimisation of both the ground and excited triplet states, place severe demands on any quantitative theoretical procedure.

Our initial studies focussed on the application of semi-empirical SCF–MO procedures as pathfinders for charting the general characteristics of such reactions. The MNDO SCF–MO method [7] has been extensively evaluated for a wide range of properties, including adiabatic singlet and triplet excitation energies. Although these are predicted to be generally too low [8] by *ca.* 1 eV, the geometrical changes associated with excitation were found to be qualitatively reasonable.[8a] A recent MNDO (and AM1) study of the (S_1–S_0) adiabatic energy gap in a series of primary amines revealed an average error (0.42 eV) to be significantly smaller for this specific series.[8b] MNDO has also proved to be useful in predicting substituent effects for reactions involving single-electron transfer and open-shell intermediates.[9] One noted defect of the MNDO method, however, is the very low hydrogen-bonding energies predicted for a range of systems, and the more recent AM1 procedure was developed with this in mind.[10] The interaction energies of simple hydrogen-bonded systems are indeed better reproduced, and the error in excitation energies is quite similar to those found for MNDO.[8] However, the AM1 method is now known to favour [11] bifurcated molecular geometries for hydrogen-bonded complexes involving oxygen, which for water dimer, at least, is certainly incorrect.[12] We have recently shown [13] that AM1 also contains a specific defect in the nitrogen parametrisation, which has the effect of overestimating core–core repulsions at distances to nitrogen of *ca.* 2.1 Å and hence, in turn the geometries of transition states and complexes involving nitrogen bonds in this region. The most recent [12] semiempirical method PM3 appears to predict geometries for neutral hydrogen-bonded complexes involving nitrogen or oxygen similar to those obtained at the *ab initio* MP2/6-31G** level.[14] However, little is known about the PM3 method in respect of triplet or excited states. In the present study, we had several objectives. Firstly, we compare both methods with regard to the gas-phase ($n = 0$) geometries and energies of the ground and excited triplet states of the $O_2 \cdot NH_3 \cdot nH_2O$ system. Secondly, we compare AM1 and PM3 solvation enthalpies and structures of the charged species NH_4^{+} and OH^{-} with known experimental values. Finally, we discuss the validity of these AM1 and PM3 models of amine photo-oxygenation in the context of known errors of the methods.

Computational Procedure.—The PM3 and AM1 calculations were carried out using the MOPAC (V5.0) [15] and AMPAC (V2.1) program systems,[16] all geometrical variables being optimised. Calculations of the different electronic states of the $NH_3 \cdots O_2$ complex were performed with the multi-electron configuration interaction facility (MECI) in either program, using the 'half-electron' open-shell approximation. An active space of four molecular orbitals was selected for the configuration interaction (CI), comprising the highest doubly occupied orbital (essentially a lone pair on nitrogen), the two singly occupied oxygen orbitals (degenerate at large N–O distances) and the lowest unoccupied molecular orbital corresponding to the first antibonding orbital of A_1 symmetry on

ammonia. For certain geometries, the initial SCF orbitals did not converge to the above, and some pyramidalisation at the nitrogen was necessary to achieve the correct reference configuration. Additionally at certain AM1 geometries the fourth active orbital would correspond to a virtual orbital on solvent water rather than ammonia; these AM1 results are excluded from the present comparisons. The active orbitals selected contain four electrons and can give rise to 36 electronic configurations (microstates) comprising 20 singlets, 15 triplets, and 1 quintet. Initially, numerical derivatives of the CI wavefunction were used with increased SCF accuracy to ensure reliable geometry convergence using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) procedure.[17] Ground, first, or second excited triplet states were calculated by selecting the appropriate root of the CI matrix for optimisation (ROOT = 1, 2, or 3 as keywords). The energy of the zwitterionic state was particularly sensitive to the separation between the ammonia and oxygen, whereas that of non-polar excited states were much less so. This was found on occasion to lead to instability in the numerical (finite difference) evaluation of geometrical derivatives and hence, the BFGS optimisation. Use of the analytical CI derivatives option[18] available in AMPAC (V2.1) resulted in more robust and significantly faster geometry optimisation ROOT = 1 only. The energies of water clusters were calculated without CI, since the excitations described above do not include water orbitals.

Results and Discussion

The Ground Triplet State T_0.—The calculated geometry of the triplet ground state of the ammonia–oxygen complex shows that the equilibrium distance between the two moieties is relatively large (*ca.* 3–4 Å) at the AM1 and PM3 level, and both the ammonia and oxygen have structures almost the same as those of the isolated molecules. The energy of the complex calculated with the components 100 Å apart shows the complexation energy to be less than 1 kcal mol^{-1}, there being no exchange stabilisation for the triplet state.[5]

The First Excited Triplet Neutral State T_N.—In the CI space we have defined, excited non-polar triplets which result in very little charge reorganisation can arise either from local excitations on the ammonia or oxygen or from the interchange of electrons between the two moieties. At the AM1 level,[8] the first such excited triplet state (T_N) is 78.1 above the ground state T_0 (Table 1). The calculated properties of this T_N state shows the electron-density distribution to correspond to a pure local excitation from the ammonia lone pair, resulting in microstates which contain all four electrons in different orbitals and can, therefore, be considered as triplet components of a genuine quintet state. As with the ground state, the T_N complex has no significant stabilisation compared with isolated O_2 and NH_3[5] and hence no efficient chemical transformation can be expected.

Table 1. Enthalpies of formation of different states of ammonia, triplet oxygen, and their complex.

	ΔH_f(AM1)[a]	ΔH_f(PM3)[a]
O_2 ($^3\Sigma g^+$)	−27.1	−4.2
NH_3 (S_0)	−7.7	−4.4
NH_3 (T_1)	70.6	60.8
NH_3 (S_1)	70.4	67.7
NH_3–O_2 (T_0)	−35.6	−8.6
NH_3–O_2 (T_N)	42.4	63.6[b]
NH_3–O_2 (T_P)	76.6	57.2, 62.5[c]

[a] kcal mol^{-1} (1 cal = 4.184 J). [b] CI Root = 2, r_{N-O} 4.8 Å. [c] CI Roots 2 and 3 respectively, r_{N-O} 2.0 Å.

At the PM3 level, the first non-polar excited, triplet state was obtained only at an equilibrium N–O separation of *ca.* 4.8 Å, similar to the AM1 value, but with a slightly lower excitation energy (72.1 kcal mol^{-1}, Table 1).

The First Excited Triplet Ionic State T_P.—The T_P state is chemically the interesting one, since subsequent hydrogen-atom abstraction reactions by the oxygen radical anion result in functionalisation of the amine component. Inspection of the triplet microstates shows that all (four) mono-excitations are actually charge-transfer electronic transitions. Two of these involve electron transfer from NH_3 to O_2, and the other two exactly the reverse. The first two mono-excitations are of lower energy owing to the greater electronegativity of oxygen, and correspond to the promotion of an electron from lone pair at NH_3 to one of the formerly singly occupied MOs on oxygen. The more stable of these microstates is the main component of the T_P electronic state at the AM1 level and is calculated to be 112.0 kcal mol^{-1} above the ground state. Almost complete (−0.89) charge transfer from the ammonia to the oxygen molecule occurs, with a correspondingly large dipole moment (μ = 9.25 D). There is significant asymmetry in the complex, illustrated by the two calculated equilibrium N–O distances of 2.32 and 2.50 Å, both much shorter than that calculated for T_N and the result of a strong electrostatic attraction between the two components. The dissociation energy to $NH_3^{+\bullet}$ and $O_2^{-\bullet}$ of 110.0 compares with a value of 116.5 kcal mol^{-1} obtained when two classical point charges are separated from *ca.* 2.5 Å to infinity, indicating that the interaction between the two components is indeed largely electrostatic.

The PM3 results are significantly different from AM1 in several respects. Firstly, if the initial starting geometry involves an N–O separation of <3 Å, the first excited triplet state was found to be T_P rather than T_N. The calculated geometry is more symmetrical with a shorter predicted N–O distance (1.91 Å) and smaller dipole moment (3.98 D) than calculated with AM1. There is also a lesser degree of calculated charge transfer to oxygen (−0.34), which corresponds to a significant degree of N–O bonding in the excited state. In agreement with this, the calculated PM3 normal vibrational modes of the exciplex T_P show the motions of the ammonia and oxygen to be strongly coupled, with the highest wavenumber vibration (4 312 cm^{-1}) corresponding to a correlated N–H and O–O stretching motion. The difference between the AM1 and PM3 geometries for T_P may be related to the features of the core–core repulsion function for nitrogen.[12] AM1 has a repulsive Gaussian function centred at 2.1 Å, to which we have attributed the highly asymmetrical AM1 potential surfaces obtained for a range of cycloaddition reactions involving nitrogen species.[13] This repulsive term may, therefore, account for the relatively large T_P N–O separation calculated using AM1. We have also previously shown[19] that PM3 gives more realistic potential-energy surfaces in the region of 2 Å than does AM1 for compounds containing bonds to nitrogen.

Significantly, the PM3 T_P–T_0 gap is much less than the AM1 value (65.8 and 112 kcal mol^{-1}, respectively), with a higher calculated dissociation energy with respect to $NH_3^{+\bullet}$ and $O_2^{-\bullet}$ of 130.0 kcal mol^{-1} (*cf.* 134.7 for separating point charges from 1.9 Å to infinity). This smaller T_P–T_0 gap is firstly due to an error[12] of 1.15 eV in the PM3 predicted first-ionisation potential for ammonia (9.7 eV), which would result in a charge-transfer energy 27 kcal mol^{-1} too low, and secondly to the AM1 error (−27 kcal mol^{-1}) in the calculated heat of formation of ($^3\Sigma_g^+$)O_2. The former error in PM3 may be traced to anomalous[14] trends in the PM3 atomic valence ionisation potentials U_{SS} and U_{PP}, which show the values for nitrogen specifically to be respectively *ca.* 12 and 4 eV less negative than expected from a smooth interpolation of the same parameters

Table 2. Calculated PM3 and AM1 solvation energies.

		PM3		AM1	
	ΔH_{sol}^{exp}	ΔH_f	Δ_{sol}	ΔH_f	Δ_{sol}
$NH_4^+ \cdot (NH_3)_n + NH_3$ [a]					
$n = 0$	−24.8 [b]	133.1	−17.3	124.6	−18.7
$n = 1$	−17.5	116.0	−14.0	103.4	−13.9
$n = 2$	−13.8	101.5	−11.4	84.8	−11.3
$n = 3$	−12.5	89.0	−9.4	68.1	−9.4
$NH_4^+ \cdot (H_2O)_n + H_2O$ [c]					
$n = 0$	−17.3 [b]	86.5	−13.5	76.0	−15.4
$n = 1$	−14.7	21.0	−12.1	2.6	−14.2
$n = 2$	−13.4	−43.2	−10.8	−68.9	−12.3
$n = 3$	−12.2	−106.1	−9.5	−139.1	−11.0
$OH^- \cdot (H_2O)_n + H_2O$ [d]					
$n = 0$	−24.0 [e]	−97.2	−26.3	−95.5	−22.2
$n = 1$	−18.0	−172.2	−21.6	−174.6	−19.9
$n = 2$	−16.0	−243.5	−17.9	−251.7	−17.9
$n = 3$	−14.0	−312.2	−15.5	−328.4	−17.4
$NH_3^{+\bullet} + H_2O$	—	132.4	−14.3	133.4	−15.6
$O_2^{-\bullet}(H_2O)_n + H_2O$					
$n = 0$		−83.2	−16.5	−99.3	−17.2
$n = 1$		−151.0	−14.4	−174.5	−16.0

[a] $\Delta H_f(NH_4^+)$ 153.4 (PM3), 150.6 (AM1), $\Delta H_f(NH_3)$ −3.1 (PM3), −7.3 (AM1). [b] J. D. Payzant, A. J. Cunningham, and P. Kebarle, *Can. J. Chem.*, 1973, **51**, 3242. [c] $\Delta H_f(H_2O)$ −53.4 (PM3), −59.2 (AM1). [d] $\Delta H_f(OH^-)$ = −17.5 (PM3), −14.1 (AM1). [e] Felix Franks, 'Water: A Comprehensive Treatise,' vol. 3, Plenum Press, New York–London, 1973, pp. 162.

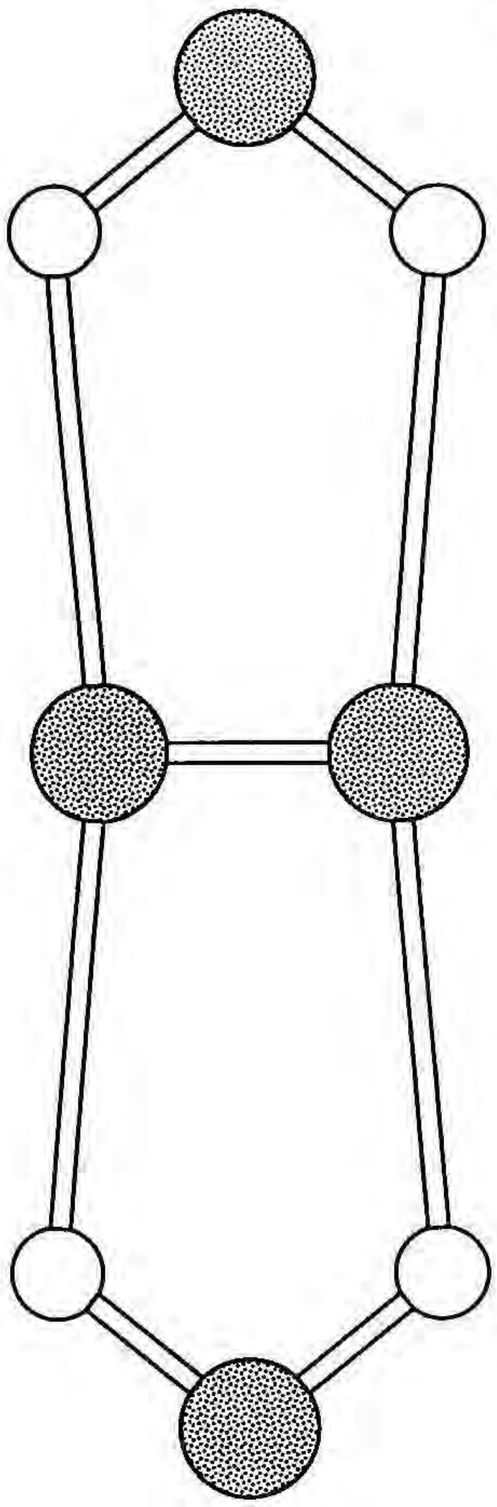
for boron to fluorine. The different errors in the PM3 s and p valence-shell ionisation potentials may in turn affect properties involving a change of hybridisation at nitrogen, as is the case when an electron is removed from pyramidal ammonia to give the planar radical cation. However, the error in the PM3 ionisation of primary substituted amines is also much reduced compared with ammonia itself,[12] which suggests that PM3 may provide a more accurate model for substituted amines than for ammonia itself.

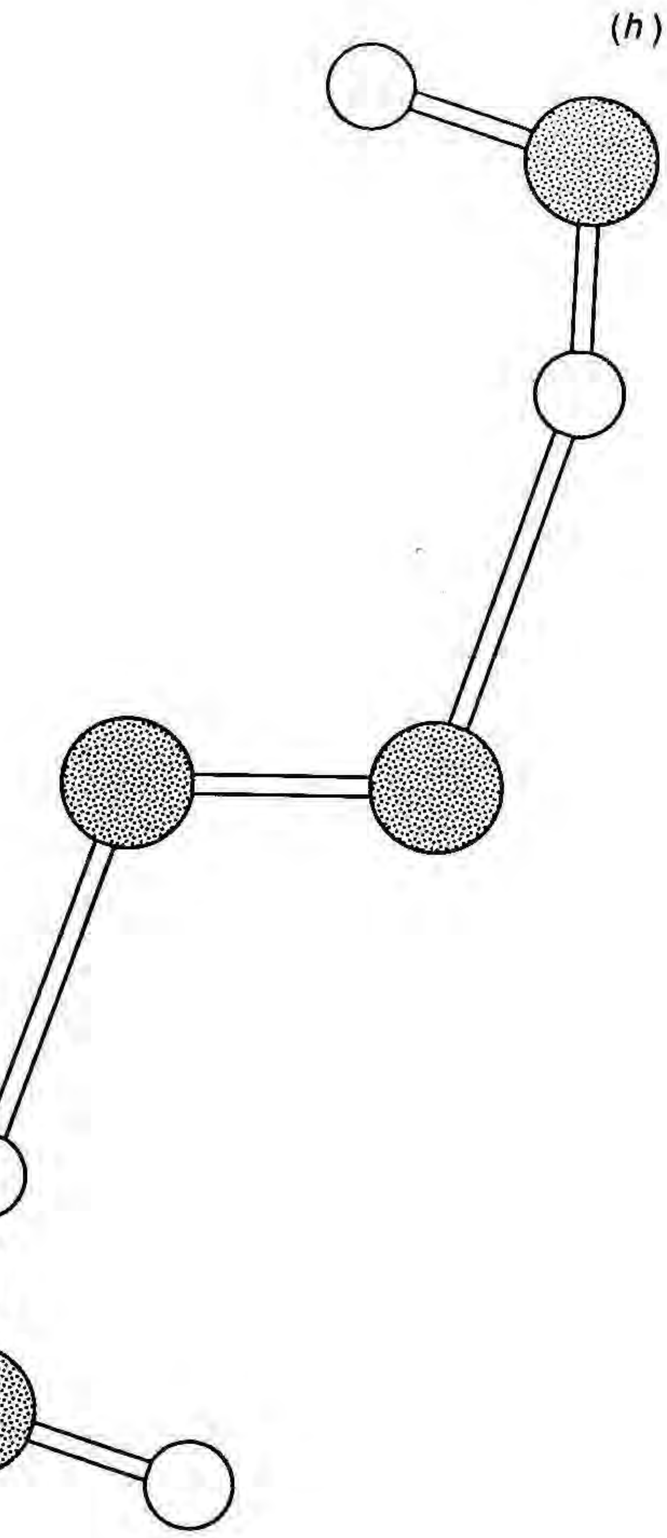
Solvation.—The relative polarity of the T_P state suggests that solvation could reduce its energy substantially compared with that of the non-polar T_N state. In an earlier paper[14] we compared both the AM1 and the PM3 methods with correlated *ab initio* calculations for the hydrogen bonding between neutral NH_3 and water. Although both methods underestimate the hydrogen-bond strength by about 2–3 kcal mol^{-1}, the PM3 method was much superior in its calculated structure, indicating that the preferred interaction is between the nitrogen lone pair and an O–H hydrogen atom. Before considering the solvation of the polar exciplex T_P, we wished to evaluate both AM1 and PM3 as models for the solvation of small related ions. Such an evaluation of AM1 for the solvation of NH_4^+ has previously been reported.[11] We now extend these results to include PM3, and additionally to the negative hydroxide anion (Table 2). Linear hydrogen bonds are found at the PM3 level (Figure 1), in which the oxygen lone pair strongly interacts with the hydrogen atom bound to nitrogen. For bonds to oxygen at the AM1 level, bifurcated structures are predicted, but where no oxygen is involved, as with $NH_4^+ \cdot 4NH_3$, AM1 and PM3 are in close agreement. This indicates that the preference for bifurcation is specifically associated with the AM1 oxygen parameters. These results indicate that a substantial degree of re-organisation in the solvent structure is required on passing from neutral $H_3N \cdots O_2$ to ionic $H_3N^{+\bullet} \cdots O_2^{-\bullet}$. Both AM1 and PM3 predict solvation enthalpies for the NH_4^+ cation which are less than the experimental values, but probably for different reasons. With AM1, the excessive core–core repulsions noted above would make such complexes too unstable, whereas with PM3, the error in the valence ionisation potentials suggests nitrogen is too electropositive. With the radical cation $NH_3^{+\bullet}$, the structural congruence between AM1 and PM3 is better, the two methods differing only in the linearity of the $O \cdots H$–N bond (Figure 1), with similar hydrogen bonding energies to the ammonium cation.

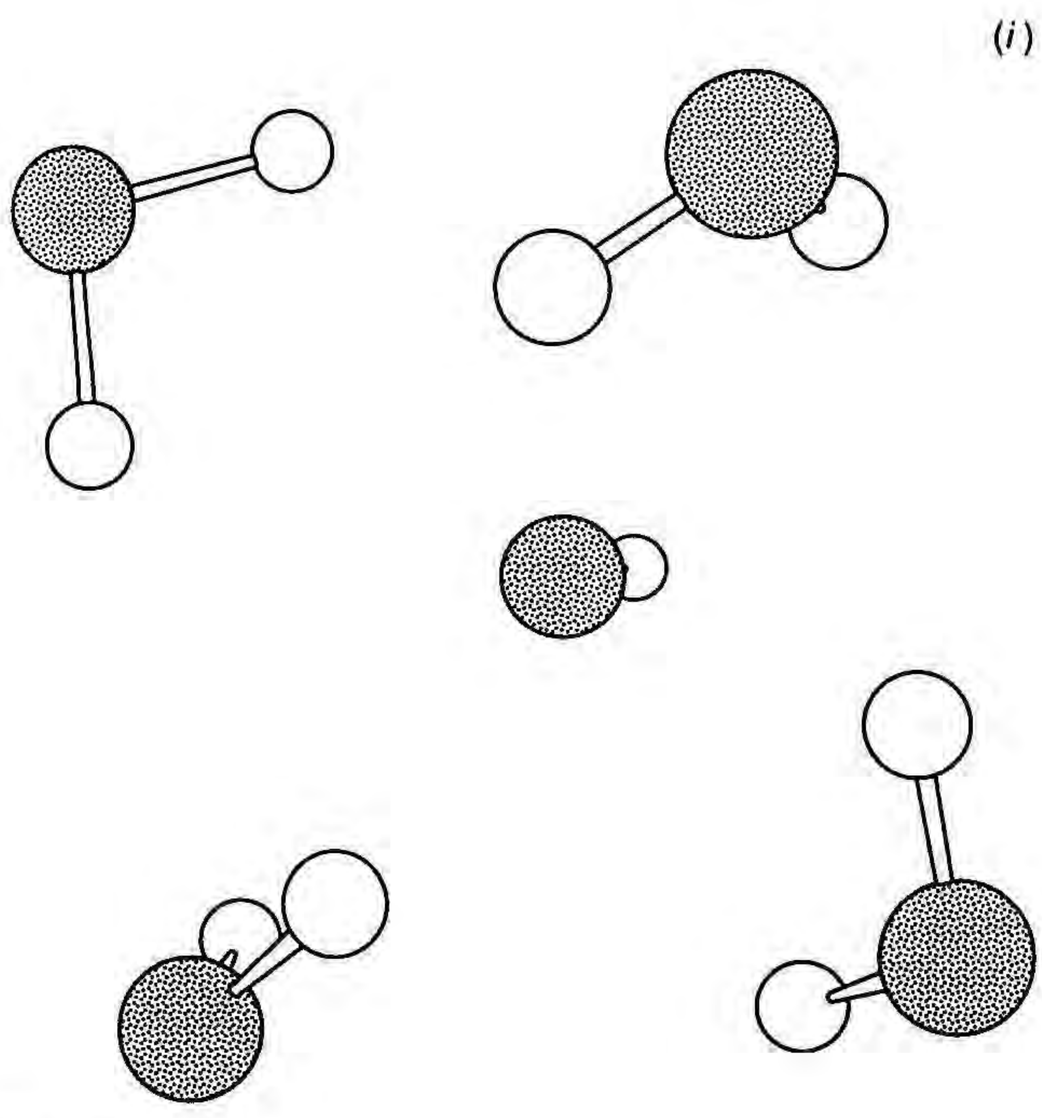
Hydroxide anion shows calculated solvation enthalpies slightly greater than experimental values (Table 2), with AM1 and PM3 structures (Figure 1) in which all four water molecules are equivalent, and (for PM3) almost linear hydrogen bonds of length 1.72 Å. The results for the radical anion complexes $O_2^{-\bullet} \cdot H_2O$ and $O_2^{-\bullet} \cdot 2H_2O$ are similar, PM3 again predicting linear bonds comparable to bifurcated structures at the AM1 level. With the neutral system $O_2(^3\Sigma_g^+) \cdot H_2O$, PM3 predicts a weak complex with an $O \cdots H$ bond length of 1.83 Å, but this system was 1.1 kcal mol^{-1} higher in energy than the separated components, indicating as expected no significant solvation for triplet oxygen.

These comparisons with experiment indicate that the energy of the gas-phase ionic state T_P is respectively over- and under-estimated at the AM1 and PM3 levels. The geometries and energies of $T_P \cdot 5H_2O$ in the ground and excited states (Table 3 and Figures 2 and 3) reveal that at the AM1 level, T_P remains above T_N in energy for one or two water molecules, but that for three or more water molecules, T_P now represents the first excited triplet state. This is due to the much greater solvation energy for T_P than for T_N (Table 3). No intersection between the ground and excited triplet surfaces was located. The AM1 calculated structure of T_P with five water molecules is highly ordered, containing a number of bifurcated hydrogen bonds similar to those found previously.[11,14] Solvation with five water molecules reduces $\Delta H(T_P–T_0)$ from 112 to 70 kcal mol^{-1} and the degree of N to O electron transfer to −0.67. The N–O distances (2.71, 2.60 Å) increase slightly compared with the gas-phase structure. Larger clusters of water molecules were beyond

Figure 1. (*a*) AM1 and (*b*) PM3 calculated structures for the hydrogen-bonded complexes $NH_4^+ \cdot 4H_2O$; (*c*) and (*d*) for $NH_4^+ \cdot 4NH_3$; (*e*) and (*f*) for $NH_3^{+\bullet} \cdot H_2O$; (*g*) and (*h*) for $O_2^{-\bullet} \cdot 2H_2O$; (*i*) and (*j*) for $HO^- \cdot 4H_2O$.







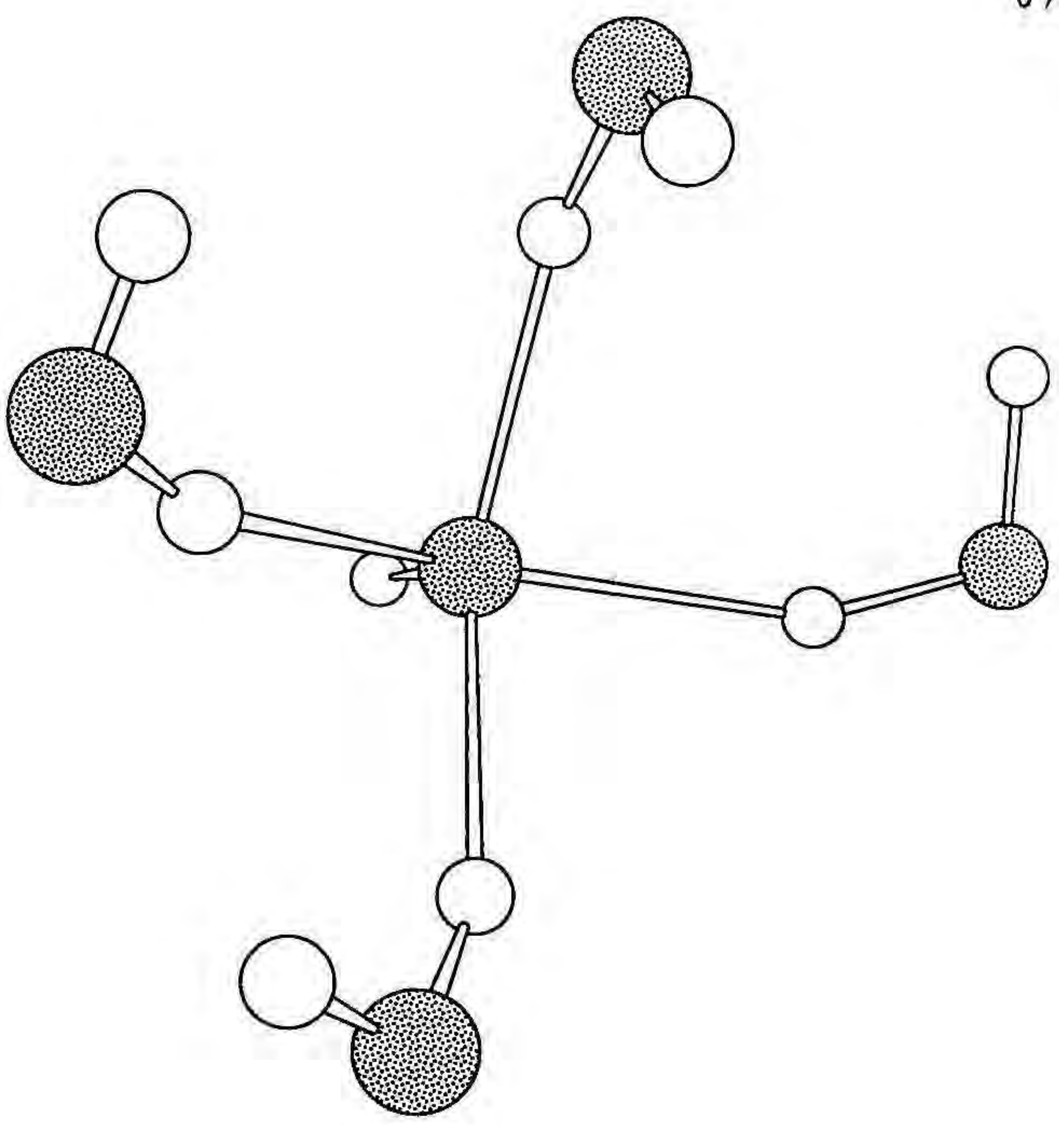


Figure 1. *Contd.*

Table 3. Energies of excited states T_N and T_P for $NH_3 \cdot O_2 \cdot nH_2O$.

n	$\Delta H_f(T_N \cdot nH_2O)$	$\Delta H_f(T_P \cdot nH_2O)$	$\Delta H_f(T_N - nH_2O - T_N^0)$	$\Delta H_f(T_N - nH_2O - T_P^0)$
AMI				
0	42.3	76.6	0.0	0.0
1	−19.1	1.6	1.4	−10.1
2	−84.7	−72.2	−2.9	−19.7
3	—	−144.6	—	−24.3
4	—	−214.8	—	−25.3
5	—	−289.0[a]	—	−37.5
PM3				
0	—	57.2	—	0.0
5	—	−246.0[b]	—	−15.2

[a] $5H_2O = 328.4$, $\Delta E(T_P - T_0) = 69.8$ kcal mol^{-1}. [b] $5H_2O = -288.0$, $T_0 = -276.4$, $\Delta E(T_P - T_0) = 30.4$ kcal mol^{-1}.

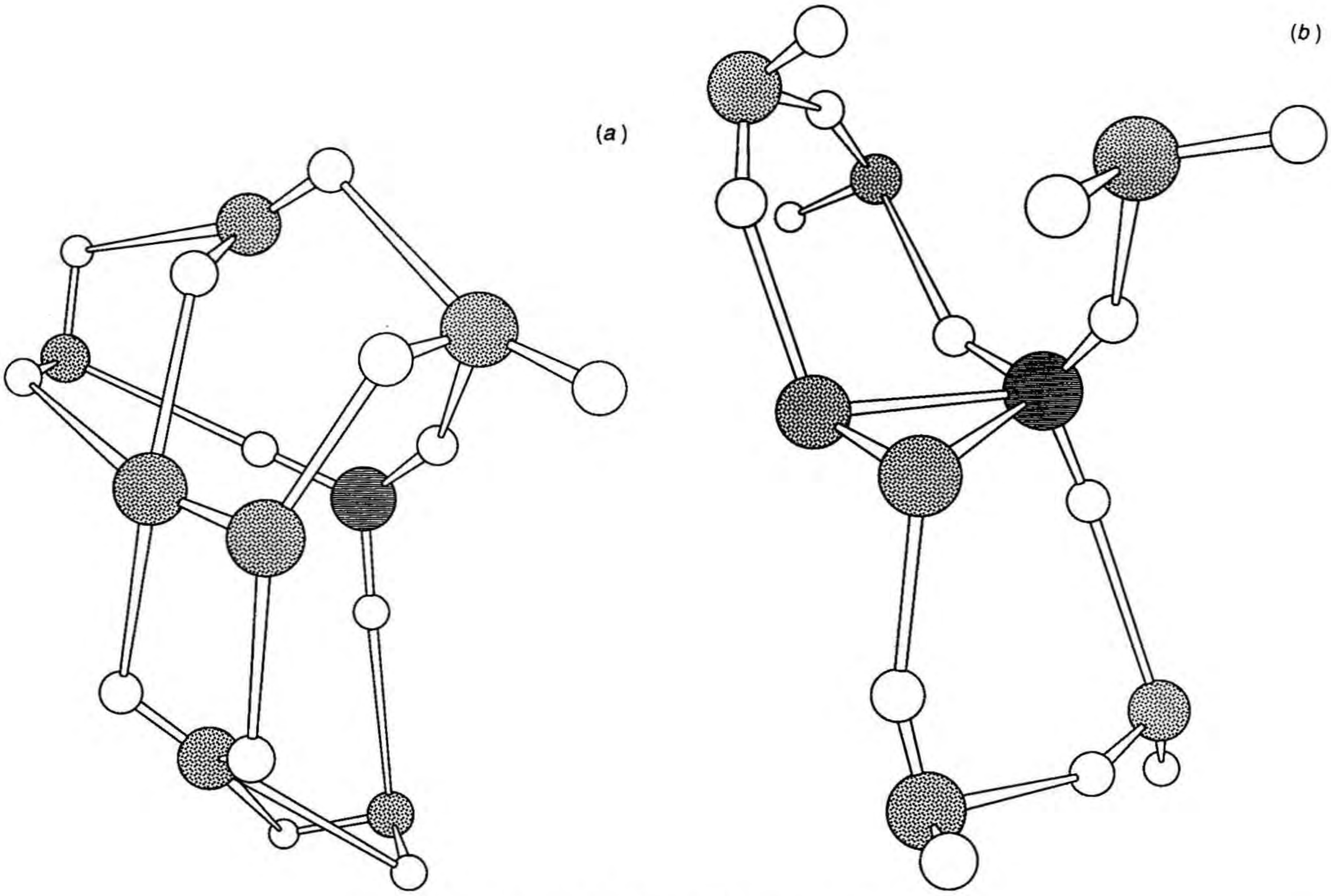
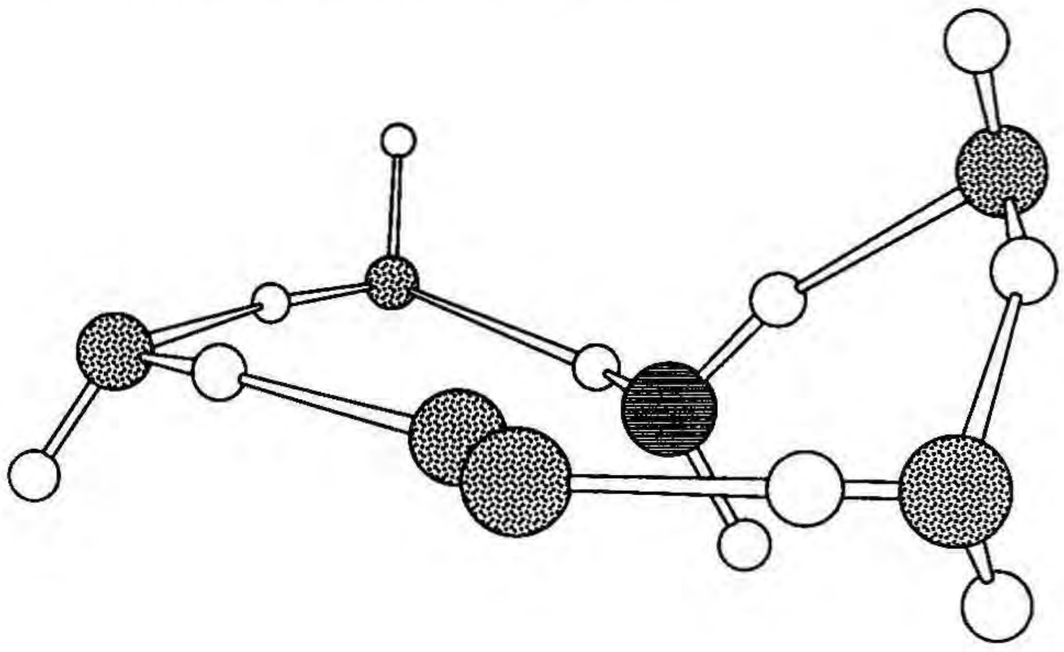


Figure 2. (*a*) AM1 and (*b*) PM3 optimised geometry of $T_P \cdot 5H_2O$.

our computational resources, but the use of analytical CI derivatives[18] should enable such models to be more readily constructed. Our experience in modelling the solvation of ground-state zwitterionic species such as glycine[20] suggests that incrementing the solvent cage from five to fifteen water molecules gains a further 8–10 kcal mol^{-1} in solvation energy.

At the PM3 level, several important differences with the AM1 results were found. At the initial (AM1) starting geometry, T_P clearly corresponded to an excited triplet state, but as optimisation proceeded, this state becomes degenerate in energy with the ground state. Redefining the required root of the CI matrix at this point enabled optimisation of $T_P \cdot 5H_2O$ as a ground triplet state (Table 3) with a calculated structure showing a cyclic system of linear hydrogen bonds involving two of the N–H groups and four water molecules forming a large ring. One of the five water molecules forms only one hydrogen bond [Figure 2(*b*)]. The additional stabilisation energy compared with isolated T_P and a cluster of five water molecules (−15.6 kcal mol^{-1}) is rather less than with AM1 (Table 3) and corresponds to only partial charge transfer, which is, nevertheless, actually enhanced compared with the gas-phase result (−0.65). The N–O distances (1.99 Å) increase slightly as a result of solvation. One more subtle change as a result of solvation is the difference in the calculated normal modes. In the absence of water, the highest energy mode corresponded to an asymmetric N–H stretch (48% energy contribution) coupled to an O–O stretch (14.5%). With five solvent molecules, the highest energy mode of 3 999 cm^{-1} comprises pure O–H stretching vibrations. The solvated mode most closely analogous to the gas-phase O–O stretching mode has a much smaller corresponding wave-



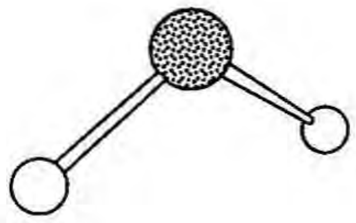


Figure 3. PM3 optimised geometry of $T_0 \cdot 5H_2O$.

number of 1 438 cm^{-1}, the O–O component (21.6%) being coupled to N–O stretches (25.5 and 12.5%) rather than N–H stretches.

The origins of the different behaviour of PM3 and AM1 can again be traced in part to the excessive nitrogen core–core repulsion found for AM1. This has the effect of increasing the equilibrium N–O separation in $T_P \cdot 5H_2O$, thus preventing any intersection of the T_0 and T_P potential surfaces. At the PM3 level, the equilibrium N–O distance of about 2 Å for T_P corresponds to a relatively high energy region of the T_0 surface, and the additional stabilisation of T_P with five water molecules is sufficient to lower the energy of $T_P \cdot 5H_2O$ to below that of T_0.

Geometry optimisation starting from the T_P geometry, but with a slightly increased N–O distance, results in a ground-state species in which no charge transfer has occurred (T_0, Figure 3). The energy (−276.4 kcal mol^{-1}) corresponds to a T_P–T_0 gap of 30.0 kcal mol^{-1}, compared with 65.8 calculated without solvent. In part this is due to the stabilisation of −15.6 kcal mol^{-1} noted above for T_P, but a similar contribution (20.2 kcal mol^{-1}) is due to an apparent destabilisation of the NH_3–$O_2 \cdot 5H_2O$ cluster compared with an isolated cluster of five water molecules and ground state NH_3–O_2 (−288.0 and −8.6 kcal mol^{-1} respectively). The geometry is certainly a local minimum in the potential surface, but does not involve formation of the most stable form of hydrogen bonding between the ammonia and water [*cf.* Table 2 and Figure 2(*b*)]. Clearly, hydrogen bonds formed within pure water clusters result in significantly more stabilisation. It is apparent, therefore, that on passing from T_0 to T_P, substantial reorganisation of the solvent cage occurs.

Conclusions

Our results for the model system NH_3–O_2 show that the PM3 semiempirical procedure provides a more realistic model for solvated excited state triplet complexes between oxygen and an amine electron donor than the earlier AM1 method, particularly with regard to the complex hydrogen-bonding structure. The inclusion of five water molecules as a model for solvation gives significant stabilisation of the charge-transfer interaction, and results (with PM3 only) in an intersection of the excited and triplet surfaces at intermediate N–O distances. The PM3 charge-transfer energy may be significantly underestimated because of a large error in the calculated ionisation potential of ammonia specifically, but this error is likely to be much smaller for mono- or di-substituted amines. Amines in which the radical cation centre can be significantly stabilised would be expected to result in proportionately more stable charge transfer complexes, and such reactions may indeed be accessible *via* thermal rather than photochemical excitation, resulting in the phenomenon known as 'dark oxygenation'. Numerous examples of such oxygenation, most frequently involving cyclic amides[6] are known experimentally, and with the introduction of analytical CI derivatives,[18] the modelling of such systems appears entirely feasible.

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