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An *ab initio* Study of the Effect of the 3*d* Orbitals of Phosphorus on the Properties of the Phosphate Group

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A large number of properties of the dimethylphosphate anion (DMP$^-$), model system for the phosphate group of the nucleic acids and the phospholipid components of membranes, has been investigated by the SCF *ab initio* procedure including the 3*d* orbitals of the phosphorus atom in the gaussian basis set and the results of the computations were compared with similar results obtained previously without taking these orbitals into account. The properties investigated include the conformational states of DMP with respect to the torsion about the P–O$_{\text{ester}}$ bonds, the distribution of the electronic charges, the molecular electrostatic potentials generated by DMP$^-$, the characteristics of the molecular orbitals, particularly the electronic isodensity maps, the hydration scheme. Qualitatively, the introduction of the 3*d* orbitals modifies little the general aspects of the results obtained for most of the properties studied. On the quantitative level significant, although generally not great, modifications may be noticed with respect to some features of these properties. One of the strongest influences of the introduction of the 3*d* orbitals concerns the decrease of the net electronic charges in DMP$^-$.

Key words: Dimethylphosphate – Nucleic acids – Phospholipids

1. Introduction

In a series of papers [1–5] we have investigated extensively by *ab initio* procedures the conformational properties, the electrostatic potential and the hydration scheme of the dimethylphosphate anion (DMP$^-$) considered as a model compound for the phosphate group of nucleic acids and the phospholipid components of membranes. In all these previous studies we have neglected the *d* orbitals of the second-row atom in the Gaussian basis set. The present paper is devoted to the examination of the effect of the inclusion of these orbitals upon the afore-mentioned properties and on the main essential structural characteristics of the phosphate group in the same model compound.

2. Procedure

The numbering adopted for the dimethylphosphate anion is recalled in Fig. 1. For easy recognition, the anionic oxygens carry the odd and the ester oxygens the even numbers.

For the sake of continuity and easy comparison with the previous studies, we have used two sets of geometrical parameters (bond length and angles). The

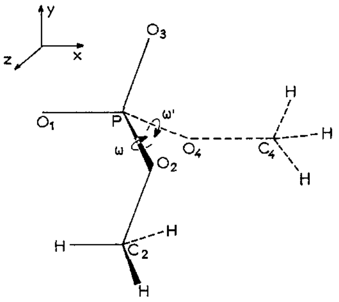

Fig. 1. Numbering and torsion angles adopted for dimethylphosphate

geometry adopted in the study of the conformational properties is the same as that used in Refs. [1, 2]; the geometry used in the remaining parts of this paper is identical to that used in Refs. [3–5].

The *ab initio* wave function of the molecule has been obtained by an SCF LCAO procedure using a modified version [6] of the IBMOL program [7, 8]. The STO 3G basis [9, 10] used in our previous computations [3, 4] was augmented by a set of 6 *d* gaussian orbitals on the phosphorus atom with exponents chosen as follows: the 3*d* Slater orbital (STO) exponent of the phosphorus atom $\zeta_{3d}(P)$, has been calculated from the 3*s* STO exponent of this atom, $\zeta_{3s}(P)$, by the approximate formula [12]: $\zeta_{3d}(P)=0.9\zeta_{3s}(P)$, yielding the value $\zeta_{3d}(P)=1.71$ when $\zeta_{3s}(P)=1.9$ (average molecule-optimized value [10]). The 3*d* gaussian orbital exponent (ξ_{3d}) has been calculated as a function of the corresponding 3*d* Slater orbital exponent (ζ_{3d}) by Huzinaga's formula [13]:

$$\xi_{3d}=\alpha\zeta_{3d}^2$$

A value of $\alpha=0.1302$ has been adopted following the data given by Huzinaga [13] for such an expansion. The resulting value of ξ_{3d} which has been retained in our computations is then $\xi_{3d}=0.4$.

We used as starting vectors in the SCF procedure the *ab initio* wave functions obtained in our previous computations without the inclusion of the *d* orbitals with the program Gauss 70 [11].

The molecular electrostatic potential has been computed from the *ab initio* wave function, as indicated in reference [14], with a program kindly communicated to us by the authors [15]. We have included into this program the computations of isodensity contours.

3. Results and Discussion

We shall examine in successive order (1) the conformations with respect to rotation about the PO bonds, (2) the electronic charge distribution, (3) the molecular electrostatic potential, (4) the energies of the molecular orbitals and their electron distribution, (5) the hydration scheme.

Table 1. Relative energies of different conformations of DMP^- (with the most stable conformation taken as energy zero)

ω	ω'	*d* orbitals not included ΔE (kcal/mole)	*d* orbitals included ΔE (kcal/mole)
270°	270°	0.	0.
180°	180°	6.8	10.0
270°	90°	1.2	1.5
300°	180°	2.6	3.0

3.1. Conformational States of DMP^-

We are concerned here essentially with the torsion angles about the O_2–P and P–O_4 bonds, for which we shall use the simplified notation, popular in the conformational studies on nucleic acids: ω and ω'. We recall only that the zero value of these angles corresponds to the *cis*-planar arrangement of bonds C_2–O_2 and P–O_4 for ω and O_2–P and O_4–C_4 for ω' and that the positive angles correspond to a right-handed rotation of the far bond with respect to the near one (see e.g. 2, 5).

Because of the large computational time required in the *ab initio* calculations, we did not construct complete conformational energy maps but have considered only a few particularly representative conformations, mainly the gauche-gauche (*gg*), gauche-trans (*gt*) and trans-trans (*tt*) ones. The terminal methyl groups have been fixed in a staggered arrangement. The comparison of the results obtained without [16] and with the inclusion of 3*d* orbitals in the computations is presented in Table 1. Its essential feature is to indicate that the conformational preferences of the dimethylphosphate ion remain qualitatively the same in both cases. The *gg* conformation ($\omega, \omega' = 270°, 270°$)[1] is still the preferred one, and this preference is even increased comparatively to the other conformations when the 3*d* orbitals are taken into account. In fact the main effect of the inclusion of 3*d* orbitals in the basis set is to increase appreciably the relative energy of the fully extended conformation ($\omega, \omega' = 180°, 180°$) which is already a high energy conformation in the computations performed without the 3*d* functions.

CNDO conformational maps of DMP^- with and without *d* electrons [16] were found similar to one another, favoring also the *gg* conformer. On the other hand, it is worth recalling that computations using empirical potentials performed on compounds containing the phosphate group [17–19] have failed to predict the *gg* conformation as the most favored one and predict the fully extended one as a low or even the lowest energy conformation.

3.2. The Electronic Charges

We give in Table 2 a comparison of the net atomic charges of DMP^- (obtained from a Mulliken population analysis [20]) in the *gg* and *tt* conformations computed

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[1] The *gg*-minimum in Ref. [16] covers a broad region of $\omega = \omega' = 270$–$300°$.

Table 2. Net atomic charges of DMP$^-$ in the *gg* and *tt* conformations[a]

Conformations		Net charges										3*d* total population
		Without 3*d* orbitals					With 3*d* orbitals					
ω	*ω′*	O_1	O_2	P	C	3H[b]	O_1	O_2	P	C	3H[b]	
270°	270° (*gg*)	−0.743	−0.475	1.352	−0.151	0.193	−0.495	−0.340	0.517	−0.134	0.210(5)	1.092
180°	180° (*tt*)	−0.757	−0.477	1.360	−0.147	0.201	−0.511	−0.349	0.534	−0.129	0.222	1.082
	Δq(*gg*-*tt*)	0.014	0.002	−0.008	−0.004	−0.008	0.016	0.009	−0.017	−0.005	−0.011(5)	+0.010

[a] These charges correspond to the geometry of Refs. [1–2]. For the geometry used on the hydration study, the *gg* charges with 3*d* orbitals are −0.509, −0.322, 0.509, and −0.144 for O_1, O_2, P and C, respectively

[b] Total for the three methyl hydrogens.

both with and without the 3*d* functions. This enables a simultaneous estimation of the effect upon electronic charges of differences in conformational states and of the inclusion of the *d* orbitals.

It may be seen that the major effect of the 3*d* orbitals is to decrease substantially both the net positive charge on the phosphorus and the net negative charges on the oxygens. The carbon atoms become somewhat less negative. Only the methyl hydrogens increase their net charges. This overall smoothing out of the net charge distribution has been made possible by a concomittant substantial accumulation of population in the 3*d* orbitals of phosphorus, as seen in the right-hand side of Table 2. These effects seem to be a general feature in compounds where the participation of the 3*d* orbitals is required to represent properly the valence of the atom in the compound considered [21] as indicated by *ab initio* [22–26], CNDO [27, 28] and even EHT computations [23, 29].

To what an extent such drastic modifications in the net atomic charges modify the molecular behavior will be seen in more details in sections 3.3 and 3.5.

Before going into this problem, let us note that the effect of conformational changes upon the charge distribution is small (Table 2). The difference between the positive (P) and negative (O) charges is, however, larger in the fully extended conformation than in the *gg* conformation in both types of *ab initio* calculations. We have indicated by Δq (*gg-gt*), in Table 2, the differences between the net charges of each atom corresponding to the two conformations. It may be seen that the values of Δq become larger when the 3*d* functions are included in the basis set comparatively to the values obtained without this inclusion.

3.3. Molecular Electrostatic Potentials

In this and the following sections the torsion angles ω and ω' have been given both the value 300° representing the most stable *gg* conformation of DMP^- adopted in the previous studies [3–5] of the same properties. The terminal methyl groups have been fixed in a staggered arrangement. Because of the two-fold symmetry of the molecule (Fig. 1) the planes O_1PO_4 and O_3PO_2 are equivalent and the same is true for the planes O_1PO_2 and O_3PO_4.

Molecular isopotential maps have been drawn in three planes: O_1PO_3 which contains the two equivalent anionic oxygens, O_1PO_2 and O_3PO_2 which contain simultaneously one anionic and one esteric oxygen. We present here (Fig. 2) only the isopotential map constructed in the plane O_1PO_3 as the conclusions which can be drawn from the comparison of this map with the corresponding one (Fig. 2) of Ref. [3] apply quite similarly to the maps constructed in the other OPO planes.

The comparison of the results of Fig. 2 of this paper (*d* orbitals included) with those of Fig. 2 of Ref. [3] (*d* orbitals neglected) shows a far-reaching general qualitative similarity. A more quantitative examination of the results leads to the following observations: (1) The numerical values of the electrostatic potentials corresponding to the different minima are lower when the *d* orbitals are included in the computations. The lowering is of the order of 7 to 9% depending on the location of these minima. (2) The distances between the minima and the anionic oxygens are slightly longer when the *d* functions are included in the computations.

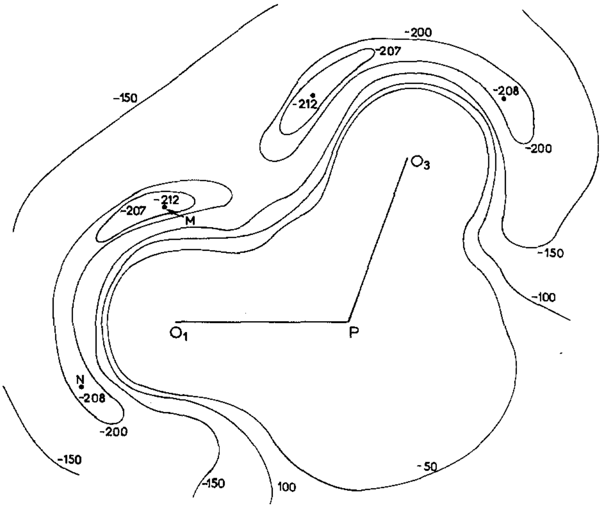

Fig. 2. Isopotential curves in the plane O_1PO_3, the 3*d* orbitals being included in the basis set (values in kcal/mole)

Thus the distance between O_1 and minimum *M* in Fig. 2 is about 0.99 Å instead of 0.95 Å in Ref. [3]. Similarly the distance O_1N is equal to 0.97 Å instead of 0.91 Å. It is to be expected that the hydration sites will also be more distant from DMP^- as a consequence of the inclusion of *d* orbitals (see section 3.5). (3) The minimum *M* (inside the O_1PO_3 angle) is situated in a direction forming an angle of 97° with the PO_1 axis. Similarly the direction of the minimum *N* (external to the O_1PO_3 angle) is at an angle of 146° with respect to this axis. These values differ significantly from 120°, the common value obtained without the inclusion of *d* orbitals. The effect of the *d* orbitals is thus to rotate the areas of strong electrostatic potential around the anionic oxygens towards the interior of the angle O_1PO_3.

In spite of the above-mentioned changes, the conclusion of Ref. [3] that the most attractive regions towards a unit positive charge are forming two circular furrows around the anionic oxygens remains valid: the electrostatic potentials in these annular regions remain within 5% of the maximum which is now -212 kcal/mole. This conclusion was reached by computing the isopotential maps in four planes defined as follows: two planes containing respectively the points *M* or *N* (Fig. 2), and perpendicular to the O_1P axis, one containing the segment *MN* and perpendicular to the plane O_1PO_3 and the last one containing the middle point of *MN* and perpendicular to the O_1P axis. The planes containing the most negative potentials are not perpendicular to the O_1P (or O_3P) axis but are shifted towards the interior of the angle O_1PO_3 as indicated in Fig. 3. Worth noting is the fact that the deepest points are not in the plane O_1PO_3 itself but on each side of it in a distribution similar to the distribution obtained without the *d* functions [3]. This out-of-plane shift is however very small.

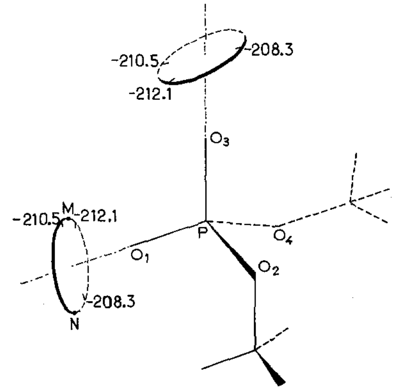

Fig. 3. The circular zone of potential around the anionic oxygens, the 3*d* orbitals being included in the basis set

On the whole, it appears that the general features concerning the electrostatic potential are not very modified by the introduction of the *d* orbitals in spite of the considerable changes observed in the gross atomic charges: even the numerical values of the potential minima are considerably less altered than one might have expected on the basis of these charges. Moreover, none of the changes observed modify any practical conclusion that could be drawn on the basis of the potential distribution computed without the *d* functions (position of the deepest potential well inside the OPO angle, much deeper potential near the anionic oxygens than near the esteric oxygens, general shape of the isopotential lines and even the order of magnitude of the minima). This appears as a far-reaching conclusion, since it shows that the essential features of the general aspect of the molecule as seen by an approaching entity are obtained with a fair accuracy by a computation without the *d* orbitals. It shows, moreover, that a quantity such as the molecular potential which is an observable directly deduced from the wave function is much less affected by the introduction of the *d* orbitals of phosphorus than the charges defined from a population analysis.

3.4. Orbital Energies and Isodensity Maps

In this section, we analyze the most important characteristics of the molecular orbitals, in particular the energies, shapes and directions of the highest occupied molecular orbitals as a function of the inclusion of the *d* functions.

Table 3 gives the energies of the 33 occupied orbitals in the two basis sets. Moreover, the relative energies of the five highest MO's are shown schematically in Fig. 4 taking as zero the energy of the highest occupied level in the computation without *d* functions. Examination of the results indicates the following main features:

(1) The participation of the *d* orbitals occurs mainly in the 10 highest occupied orbitals and in those containing the 2*s* AO's of P, O_1 and O_3; this participation is the largest in the upper four MO's.

Table 3. Energy (a.u.) and main character of the occupied orbitals of DMP^- in the two basis sets

	Without *d* orbitals		With *d* orbitals	
	-78.91414	$1s\mathrm{P}$	-78.89980	$1s\mathrm{P}$
	-20.99279	$1s\mathrm{O}_4$	-20.06082	$1s\mathrm{O}_4$
	-20.99266	$1s\mathrm{O}_5$	-20.06074	$1s\mathrm{O}_5$
	-19.67989	$1s\mathrm{O}_1$	-19.79346	$1s\mathrm{O}_1$
	-19.67953	$1s\mathrm{O}_3$	-19.79313	$1s\mathrm{O}_3$
	-10.92541	$1s\mathrm{C}_6$	-10.93501	$1s\mathrm{C}_6$
	-10.92537	$1s\mathrm{C}_7$	-10.93499	$1s\mathrm{C}_7$
	-7.20262	$2s\mathrm{P}$	-7.12012	$2s\mathrm{P}$
	-5.03051	$2x2y\mathrm{P}$	-4.95350	$2z\mathrm{P}$
	-5.03022	$2x2y\mathrm{P}$	-4.95245	$2x2y\mathrm{P}$
	-5.02998	$2z\mathrm{P}$	-4.95082	$2x2y\mathrm{P}$
	-1.14392	$2s\mathrm{O}_4\mathrm{O}_5$	-1.13285	$2s\mathrm{O}_4\mathrm{O}_5$
	-1.08821	$2s\mathrm{O}_4\mathrm{O}_5$	-1.08919	$2s\mathrm{O}_4\mathrm{O}_5$
	-0.92774	$2s\mathrm{O}_1\mathrm{O}_3$	-0.91858^{a}	$2s\mathrm{O}_1\mathrm{O}_3$
	-0.84957	$2s\mathrm{O}_1\mathrm{O}_3$	-0.85240^{a}	$2s\mathrm{O}_1\mathrm{O}_3$
	-0.77114	$2s\mathrm{C}_6\mathrm{C}_7$	-0.77137	$2s\mathrm{C}_6\mathrm{C}_7$
	-0.76749		-0.76811	
	-0.50021		-0.49808	
	-0.46295		-0.46562	
	-0.45981		-0.46237	
	-0.44346		-0.44511	
	-0.41318		-0.41067	
	-0.39291		-0.39044	
	-0.25490		-0.26738	
	-0.24870		-0.25339^{a}	
	-0.22095		-0.23191^{a}	
	-0.16170		-0.17138^{a}	
	-0.13696		-0.16546^{a}	
	-0.07374	$sy\mathrm{O}_1\mathrm{O}_3 3x3y\mathrm{P}$	-0.09600^{a}	$sx\mathrm{O}_1 sy\mathrm{O}_3 3x3y\mathrm{P}$
	-0.01797	$z\mathrm{O}_1\mathrm{O}_3 3z\mathrm{P}$	-0.05574^{b}	$y\mathrm{O}_1 xy\mathrm{O}_3 3s\mathrm{P}$
	$+0.01236$	$xy\mathrm{O}_1\mathrm{O}_3 3s\mathrm{P}$	-0.04933^{b}	$z\mathrm{O}_1\mathrm{O}_3 3z\mathrm{P}$
	$+0.03410$	$z\mathrm{O}_1\mathrm{O}_3$	-0.00468^{b}	$z\mathrm{O}_1\mathrm{O}_3$
	$+0.04855$	$x\mathrm{O}_3 xy\mathrm{O}_1$	$+0.02440^{b}$	$x\mathrm{O}_3 xy\mathrm{O}_1$
Total molecular energy (a.u.)	-710.21745		-710.69283	

[a] at least one *d* coefficient > 0.04 [b] at least one *d* coefficient > 0.10.

(2) The energies of the MO's become less widespread and all occupied MO's become bonding with the exception of the highest one whose energy is however lowered by 0.024 a.u.

(3) An inversion occurs in the ordering of the third and fourth highest occupied orbitals, and the 23rd (from the top) orbital (essentially $2p_z$) passes below the 24th and 25th.

We are presenting in Figs. 5a, b and 6a, b the electron density maps of orbitals corresponding, respectively, to Nos 1′, 1, 3′ and 3 of Fig. 4 drawn in the O_1PO_3 plane. These orbitals correspond predominantly to the $2p_x$ and $2p_y$ types of function. The comparison of the results presented in these figures (and also of

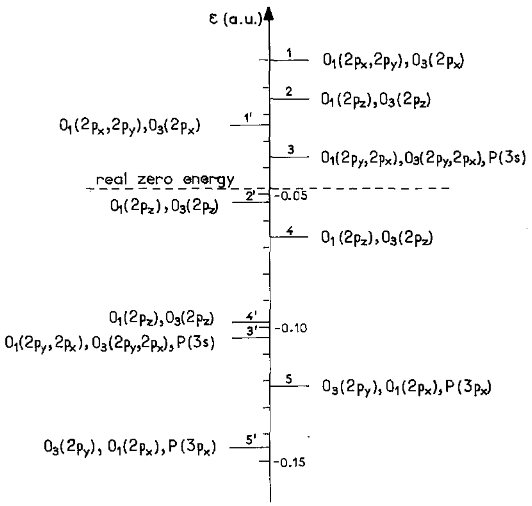

Fig. 4. Relative energies of the highest occupied orbitals in dimethylphosphate (values in a.u.) The left-hand side of the figure corresponds to results with the 3*d* orbitals included in the basis set, the right-hand side to the 3*d* orbitals neglected

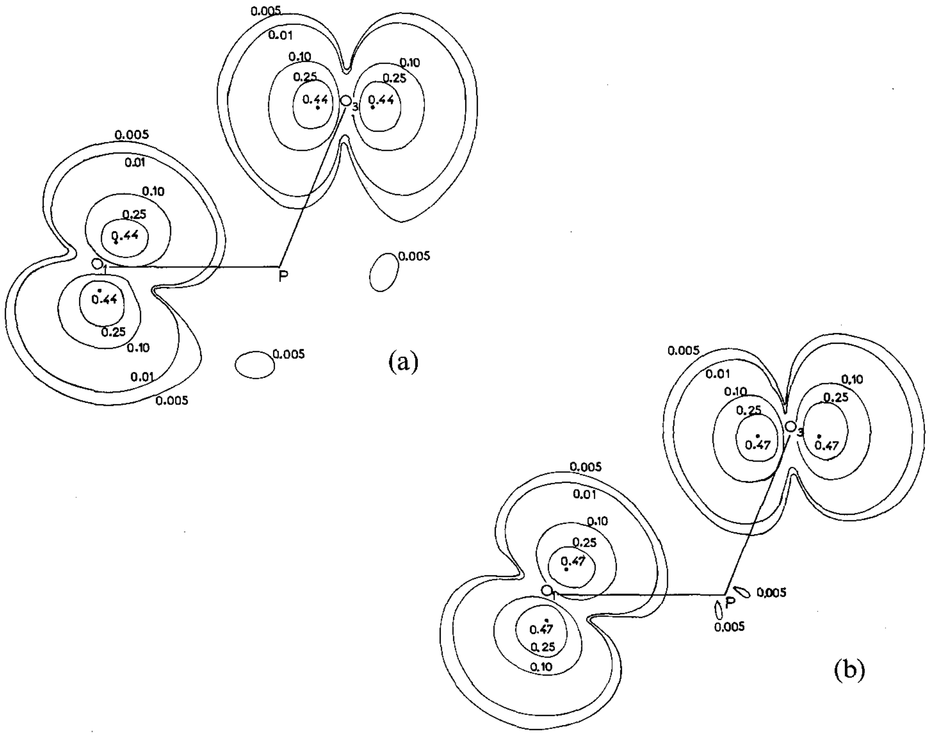

Fig. 5. Electron isodensity curves in the plane O_1PO_3 of the molecular orbitals corresponding to a) N° 1' and b) N° 1 of Fig. 4

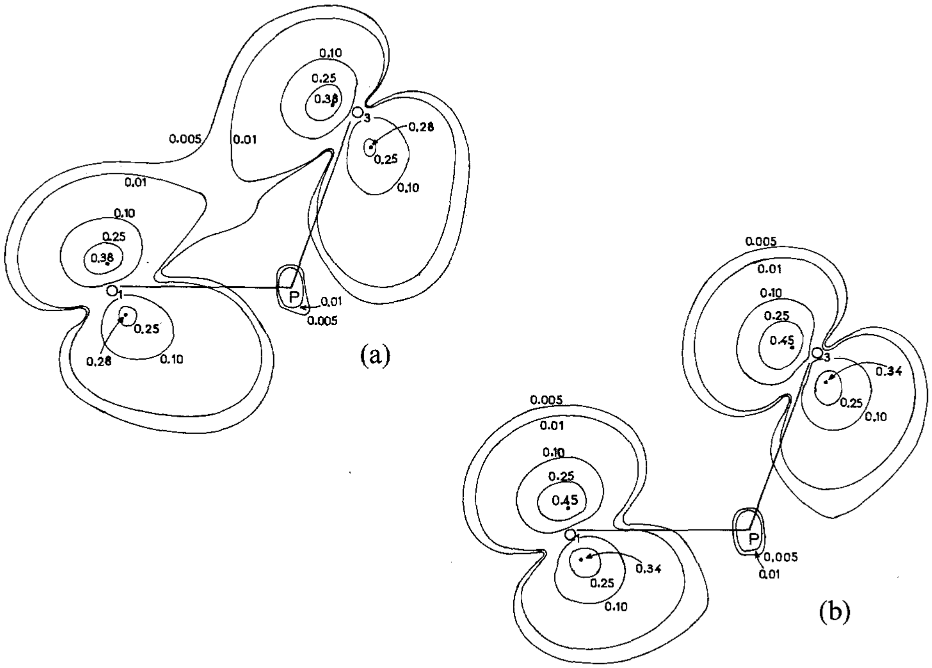

Fig. 6. Electron isodensity curves in the plane O_1PO_3 of the molecular orbitals corresponding to a) N° 3′ and b) N° 3 of Fig. 4

similar results obtained for the other orbitals not presented here) indicates that the maximum electron densities of all molecular orbitals are slightly less when the 3*d* functions are included in the basis set. These functions have little effect on the direction of the orbitals. The two *p* orbital densities around the atoms O_1 and O_3 of Fig. 6b are joined in Fig. 6a. The *z* orbitals 22′, 44′ are very similar in shape with and without *d* functions.

3.5. The Hydration Scheme

The principal hydration scheme of DMP^- determined in the previous article [4] in the absence of *d* orbitals has been reexamined by including the 3*d* functions in the basis set. The comparison of previous and present results is given in Table 4. The symbols used are the same as those in Ref. [4]. The comparison shows that one of the major effects of the inclusion of 3*d* functions is the decrease of interaction energies (ΔE) between the water molecule and DMP^- by approximately 20% (28% in the case of the site B_{13}) with respect to the energies obtained without these functions. The hydration sites E_{13} and E_{31} remain the preferred ones. The importance of the B_{13} site is decreased somewhat more, due to the effect of the 3*d* orbitals, so that it becomes energetically slightly less preferred than the sites E'_{32} and E'_{12}. We examined the water binding aptitude of a new position, E''_{13}, corresponding to an angle $\Theta = 97°$ (in the direction of the potential minimum

Table 4. Hydration of DMP^- (STO 3G, with and without inclusion of 3*d* functions in the basis set)[a]

Plane	Symbol	$d_{O...H}$(Å)	$\theta°$	$\beta°$	$-\Delta E$ (kcal/mole)		$\delta(\Delta E)$[b] (kcal/mole)
					3*d* functions not included	3*d* functions included	
O_1PO_3	E_{13}, E_{31}	1.45	120	180	28.6[c]	22.4	
		1.50	120	180	28.3	22.7[c]	5.9
		1.55	120	180	27.6	22.5	
	B_{13}	1.75	110	143	27.1[c]	19.3	
		1.80	110	143	26.7	19.6[c]	7.5
		1.85	110	143	26.0	19.5	
	E''_{13}	1.55	97	180	24.4	18.9	—
		1.50	120	180	27.4[c]	—	
O_3PO_2	E'_{32}	1.50	120	180	26.7	—	5.9
		1.55	120	180		20.8	
O_1PO_2	E'_{12}	1.45	120	180	27.0	—	5.8
		1.50	120	180		21.2	

[a] θ = angle between PO_i and $O_i...H$ directions
β = angle between $O_i...H$ and $H\text{–}O_{water}$ directions.
The symbols E_{ij} and E'_{ij} correspond to water bound by one hydrogen bond to the oxygen *i* in the plane O_iPO_j. See text for E''_{ij}.
B_{ij} corresponds to water making a bridge between oxygens *i* and *j*.

[b] ΔE (with *d* functions) $-\Delta E$ (without *d* functions).

[c] optimal value.

M of the electrostatic potentials of section 2.3.), the hydrogen of the water molecule which is not implied in the hydrogen bonding being turned towards the interior of the angle O_1PO_3. The interaction energy corresponding to this site ($\Delta E = -18.9$ kcal/mole) is very close to the energy of B_{13} ($\Delta E = -19.6$ kcal/mole) when the 3*d* functions are included in the basis set.

This situation is comparable to the results without *d* functions where an E''_{13} site was also found in the direction of the potential minimum (this time $\Theta = 120°$) very close in energy to B_{13}.

These results show that, as suggested in Ref. [3], the disposition of the electrostatic potential minima around the anionic oxygens has a notable bearing on the positions and energies of hydration sites, and point to the fact that the electrostatic component of the interaction energy between water and DMP^- is an important one.

Another feature of the results presented in Table 4 is the increase of the equilibrium distance between water and DMP^- by an amount of 0.05 Å when the 3*d* functions are included. This feature may be related to the effect of 3*d* orbitals to displace the minima of the electrostatic potential by about 0.04 Å further away from the anionic oxygens (see section 2.3.). Note that both the decrease in the values of the binding energy and the lengthening of the distance appear as general consequences of the improvement of the basis set, particularly in ionic species [30].

The comparison of net charges in the $DMP^-...H_2O$ adduct obtained without and with *d* functions is illustrated in Figs. 7a, b, c and d on the example of the E_{31} and B_{13} sites. It is seen that the qualitative modifications of the charges of

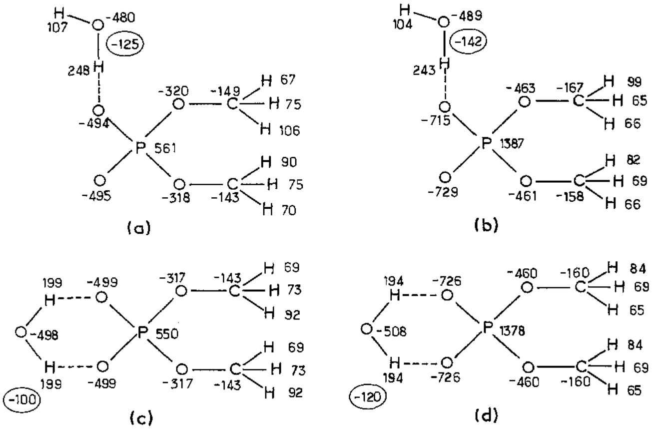

Fig. 7. Atomic net charges of the $DMP^-...H_2O$ adduct for different positions of the water molecule (in millielectron units)
a) and c): *3d* orbitals included
b) and d): *3d* orbitals neglected.
The numbers in circles represent the charge transfer to water

the two molecules upon binding are similar in the two basis sets. Moreover the quantitative modifications are not very different in spite of the appreciable modifications brought about in the phosphate itself by the *d* orbitals. The global charge transfer is decreased from 0.142 to 0.125 e in E'_{13}, from 0.120 to 0.100 e in the bridged site.

The negative character of the oxygen of the bound water molecule remains very large, particularly in the bridge position. It seems likely that this partial anionic character acquired by water should make it apt to bind further water molecules in a second hydration shell as was found in the computation without *d* functions.

We have thus analyzed this possibility with the present basis set. For this sake we have considered the model indicated in Fig. 8: the first water molecule (W1) is in a bridge position in the O_1PO_3 plane (B_{13}), the distance O...H(W1) being 1.80 Å; the second water molecule (W2) is situated in the bisector plane of the angle O_1PO_3 with the distance O(W1)...H(W2) = 1.50 Å. The comparison of the results obtained with those obtained for the corresponding positions without inclusion of 3*d* orbitals in the basis set is presented in Table 5.

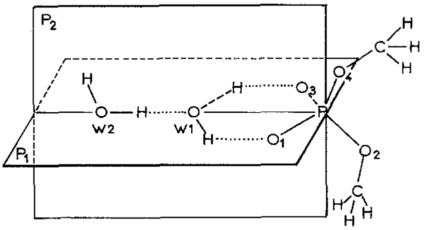

Fig. 8. Positions of the two water molecules considered in the computations

Table 5. Dihydration of DMP^- (STO 3G, with and without inclusion of 3*d* functions in the basis set)[a] (kcal/mole)

	3*d* functions included	3*d* functions not included
ΔE (total)	−38.0	−45.1
ΔE_1[b]	−19.6	−27.1
ΔE_2[b]	−18.4[c]	−18.0

[a] For the dispositions of water molecules see Fig. 8.

[b] ΔE_1 is the binding energy of the first water molecule alone;
ΔE_2 is the increment of binding energy upon fixation of the second molecule.

[c] O(W1)–H(W2) = 1.5 Å; not completely optimized.

It is seen that while the energy of binding of the first water molecule to the B_{13} site of DMP^- is significantly decreased by the inclusion of the 3*d* orbitals in the computations (from −27.1 to −19.6 kcal/mole), the energy of binding of the second water molecule is slightly increased by this refinement. The total energies of interaction of the two water molecules with DMP^- are decreased by about 15% by the inclusion of the *d* orbitals.

The reason why the binding energies of W2 are similar in both computations resides probably in the fact that this water molecule feels essentially the influence of W1 which is only slightly perturbed by the inclusion of the phosphorous 3*d* orbitals in the basis set (Fig. 7). Thus the general conclusions formulated in the previous articles [4, 5] on the number and nature of hydration sites and shells around the phosphate ion should remain essentially valid independently of the inclusion or neglect of the 3*d* orbitals of phosphorus in the basis set.

4. Conclusions

The principal conclusion of this large comparison of the properties of DMP^- as a function of the inclusion or neglect in the computations of the 3*d* orbitals of phosphorus points to the limited importance of this inclusion for the properties considered. The qualitative pictures obtained for such a large variety of properties as the preferred conformational states with respect to the torsion about the $P–O_{ester}$ bonds, the general aspect of the molecular electrostatic potentials and the location of the principal minima, the general aspects of the electronic isodensity maps and of the hydration scheme remain unchanged or are only slightly perturbed.

These properties may thus be satisfactorily explored without the explicit inclusion of *d* orbitals. On the other hand, the introduction of these orbitals has one strong incidence: a large decrease of the net electronic charges in DMP^-. This decrease has an important bearing. It points to the lack of significance of the "charges" obtained in this type of compound when the *d* orbitals are neglected.

Because of this neglect the five valence electrons of the phosphorus atom are necessarily distributed on other atoms, leading to exaggerated values of their concentrations there. For that reason one cannot compare for instance the charges on the oxygens of DMP^- computed in such a way with those of an ion involving only second row atoms, e.g. CO_2^-. The charges only become comparable when the *d* orbitals on phosphorus are taken into account. Therefore their inclusion is necessary for the study of that distribution, in so far of course, as one wants to use the concept of atomic populations.

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