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Metaphosphate and Tris(methylene)metaphosphate ($P(CH_2)_3^-$) Anions. Do They Have Three Double Bonds to Phosphorus?

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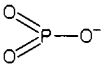
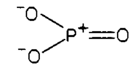
Abstract: Ab initio studies are presented for metaphosphate ion, PO_3^- (**1**), and tris(methylene)metaphosphate ion, $P(CH_2)_3^-$ (**2**). Using good basis sets at the SCF level, the minimum energy structure of **2** is a D_3 structure with the CH_2 groups twisted by 19° from the molecular plane, but this structure lies only 1 kcal mol^{-1} below the constrained D_{3h} planar structure. Inclusion of electron correlation increases this energy difference by only 1 kcal mol^{-1}. The charge distributions correspond to highly polar structures with large negative charges on the oxygens and methylene groups of PO_3^- and $P(CH_2)_3^-$, respectively. The best simple representation of these compounds is as dipolar structures; double bonding to phosphorus is relatively weak.

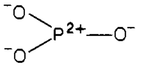
Metaphosphate ion, PO_3^- (**1**), and its methylene counterpart, $P(CH_2)_3^-$ (**2**), present interesting problems in bonding and electronic structure. The least dipolar Lewis-type structure of **1**, for example, is the hypervalent structure **1a** which formally requires



1a



1b

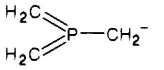


1c

expansion of the phosphorus octet, presumably with 3d orbitals. Three equivalent such structures could contribute to a resonance hybrid. An important alternative Lewis structure is the phosphonium dioxide structure **1b** in which all atoms have normal octets. Again, three equivalent such structures could contribute to a resonance hybrid.

Structure **1b** emphasizes the potential availability on the central phosphorus of a 3p orbital that could be involved in π-bonding to the oxygens. In this respect this system differs from the phosphinate-type structures we studied previously[2] in which four atoms are bonded to phosphorus. Finally, if multiple bonding is weak, structure **1c** is a highly polar Lewis structure with a phosphorus sextet similar in character to the carbonium oxide structure of a carbonyl compound, $R_2C^+-O^-$.

Metaphosphate ion plays an important role in biochemical mechanisms[3] and is a stable gas-phase species,[4] but has received only two previous ab initio studies.[5,6] The present paper also presents a detailed theoretical study of the trismethylene analogue **2**. Structure **2a** shows its formal relationship to **1a**. An important



2a

distinction is that in **2** the energy effect of the relative mutual orientation of the methylene groups can provide an important gauge of the role of π-bonding. That is, as in the accompanying paper on hypophosphite ion,[2] the structural effects of relative orientations of the methylene groups provide a measure of the electronic effects of conjugation in these systems. The study of different methylene group orientations in **2** also provides a probe for the roles of Hückel and Möbius conjugation in **1**. Note that **1** and **2** are also valence isoelectronic with trimethylenemethane dianion, the prototypical candidate for the putative Y aromaticity.[7-9] The synthesis and structure of a substituted derivative of **2** has recently been reported.[10]

Table I. Relative Energies and PC Bond Lengths for **2** (RHF/3-21+G*)

	rel energy, kcal mol^{-1}	PC bond length, Å
D_3	0.0	1.672
D_{3h}	1.0	1.672
$C_{2v}\perp$	13.4	1.667, 1.667, 1.703
$C_{2v}\perp_2$	42.1	1.651, 1.715, 1.715
$D_{3h}\perp_3$	112.0	1.725
C_{3v}	62.4	1.756
D_3(30°)	1.16	1.672
D_3(40°)	5.98	1.674

Table II. Geometries[a] and Energies[b] for the Two Lowest Energy Structures **2**-D_{3h} and **2**-D_3

basis	3-21+G*	DZ+P	DZ+Pd
		2-D_{3h}	
CH	1.078	1.076	1.077
CP	1.672	1.672	1.667
PCH	120.7	120.4	120.4
energy			
SCF	−455.535 923	−457.718 986[c]	−457.736 483
CISD		−458.216 197	
MP2		−458.376 123	
		2-D_3	
CH	1.078	1.077	1.077
CP	1.672	1.672	1.667
PCH	120.6	120.4	120.3
HCPC	20.4	18.4	19.0
energy			
SCF	−455.537 584	−457.720 150[d]	−457.737 736
CISD		−458.218 639	
MP2		−458.379 827	

[a] All bond lengths in Å and angles in degrees. [b] In hartrees, with Davidson correction for unlinked clusters for CISD. [c] ZPVE = 16 804 cm^{-1}. [d] ZPVE = 17 125 cm^{-1}.

Theoretical Approach

1 was studied theoretically with the first of the following basis sets; **2** was examined with all three.

1. 3-21+G* with sp-diffuse functions at carbon (oxygen) and d functions at all heavy atoms; the exponents were $\alpha_{sp}(C) = 0.0438$, $\alpha_d(P) = 0.55$, $\alpha_d(C) = \alpha_d(O) = 0.8$, $\alpha_{sp}(O) = 0.0845$.[11,12]

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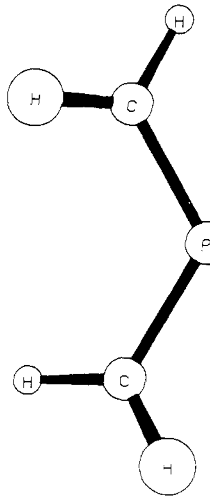

Figure 1. D_3 structure of **2**.

This basis was used for both **1** and **2**.

2\. DZ+P, a double-ζ[13] plus polarization basis set, P(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), H(4s1p/2s1p), with polarization exponents $\alpha_d(P) = 0.5$, $\alpha_d(C) = 0.75$, $\alpha_p(H) = 0.75$ (124 basis functions).

3\. DZ+Pd, double-ζ plus polarization plus diffuse functions, P(12s8p2d/7s5p2d), C(10s6p1d/5s3p1d), H(4s1p/2s1p) with $\alpha_d(P) = 1.0, 0.25$ and the exponents of the diffuse functions, $\alpha_s(C) = 0.0345$, $\alpha_p(C) = 0.0335$, $\alpha_s(P) = 0.0311$, $\alpha_p(P) = 0.0363$, chosen according to the method suggested by Lee and Schaefer.[14]

All geometries were optimized at the RHF/3-21+G* level within the given symmetries and the constaint of planar methylene groups (CHHP plane) (Table I) using analytical gradient techniques. The D_3 and planar D_{3h} structures were also optimized with the DZ+P and DZ+Pd basis sets (Table II). Harmonic frequencies were calculated for the D_3 and D_{3h} RHF/DZ+P structures using analytical second derivatives. Single-point energy calculations were performed for the RHF/DZ+P optimized structure with Moeller–Plesset (MP2) and configuration interaction (CI). The CI included all single and double excitations keeping the core orbitals doubly occupied and the corresponding virtual orbitals unoccupied; this procedure generated 105 176 configurations for **2**-D_{3h} and 198 025 configurations for **2**-$\mathbf{D_3}$.

Metaphosphate Ion (1)

The structure of **1** was optimized within D_{3h} symmetry to give a P–O bond length of 1.475 Å. Essentially the same structure was determined by O'Keeffe, Domenges, and Gibbs,[6] using a 6-31G(*) basis (d orbitals on P only; no diffuse functions). The charge distribution was determined by "integrated spatial electron populations" (ISEP),[15] calculated with PROJ,[16] and by the natural population (NP) procedure of Reed and Weinhold.[17] As mentioned in the previous paper[2] the use of a projected density function approximates the virial partitioning method of Bader[18] and the resulting "ISEP" values are approximations to true spatial integrations over Bader "basins"; that is, the Bader method is based on rigorous and well-defined partitions of the electron density function, a physical observable, with assignment of the integrated electron populations to "atoms" that have rigorously defined boundaries by the Bader approach. The Reed and Weinhold NP method is a partition of the Hilbert space to "atomic orbitals"; since it is based on natural atomic orbitals and is relatively basis set independent, it is probably the "best" (most chemically meaningful) of this type of population analysis. ISEP and NP give the formal charge at oxygen as −1.56 and −1.23, respectively, and at phosphorus +3.68 and +2.70, respectively. Such differences in magnitude are not uncommon in such comparisons[19] in which fundamentally different definitions are used for concepts that are not themselves physical observables. Much more important than the absolute numbers is the fact that both indicate a highly polar PO bond with, therefore, little double-bond character. The ISEP results for oxygen are similar to those obtained for phosphine oxide, −1.56,[20] phosphinate ion, $H_2PO_2^-$, −1.603, and methylenephosphoranyloxide ion, $CH_2PH_2O^-$, −1.624. The large charge separation in **1** suggests that any PO double bonding involved is highly polarized; such double bonding provides little charge transfer to phosphorus. A further indication that double bonding is weak comes from structure. The PO bond length of 1.47 Å in PO_3^- is about the same as that in phosphine oxide, 1.47 Å,[20] and is only 0.03 Å shorter than that in $H_2PO_2^-$.[2] In the latter two compounds any double bonding must be of the hypervalent type at phosphorus. Thus, the availability of a 3p orbital on phosphorus in PO_3^- does not result in much bond shortening; the electronic structure is accordingly most simply represented by **1c**.

These results for PO_3^- may be compared with those obtained recently for the neutral isoelectronic system $(HN)_2PNH_2$.[21] The P–NH bonds were described, primarily on the basis of Mulliken populations, as highly polar but with a significant π-bond contribution. Another related system is that of diimino- and dioxophosphorane, X_2PH (X = NH, O).[22] This system is a neutral analogue of **1** in which the comparable resonance structures are:

$$^-X{-}PH^+{=}X \qquad X{=}PH^+{-}X^- \qquad ^-X{-}PH^{2+}{-}X^-$$

These compounds were also considered, primarily on the basis of Mulliken populations, to have highly polar electronic structures with only weak π-bonding. d-Orbitals were considered not to play a large role and then primarily to polarize the σ bonds.[22] Note that the PO bond distance in dioxophosphorane, 1.435 Å, is only 0.035 Å shorter than that in PO_3^-, despite the comparison of a neutral molecule with an anion.

Thus, the primary difference between our conclusions with regard to **1** and these related structures is one of degree. The integrated population results suggest even greater charge polarization and weaker π-bonding than suggested by Mulliken populations. The nature of this comparison requires further discussion.[23] Analysis can be focused, for example, on the charge distribution within the π system. PO_3^- has three occupied π valence MO's (a_2, MO 15, and e, MOs 18 and 19; the HOMO is MO 20) that correspond to the $a_2^2e^4$ π configuration of a Y-conjugated system. The two e MOs are nonbonding with nodes at P (except for small contributions from d functions), whereas the a_2-MO is a bonding MO to which the P 3p orbital can contribute. Mulliken population analysis of this MO, the only π-bonding MO that corresponds to PO double bonding, assigns populations of P, 0.8, and O, 0.4. At first sight this analysis implies

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Table III. Natural Populations (NP) for **1** and **2** (RHF/3-21+G*)

	total NP		NAO populations	
	P	O	$3p_\pi(P)$	$2p_\pi(O)$
1	12.30	9.23	0.56	1.79

		total NP				NAO populations	
		P	C	C	C	$3p_\pi(P)$	$2p_\pi(C)$
2	D_3	13.33	7.34	7.34	7.34	0.89	
	D_{3h}	13.30	7.35	7.35	7.35	0.88	1.69
	$C_{2v}\perp$	13.35	7.45	7.27	7.27	0.86	1.56
	$C_{2v}\perp_2$	13.37	6.99	7.48	7.48	0.80	1.20
	$D_{3h}\perp_3$	14.38	6.89	6.89	6.89	1.81	
	C_{3v}	14.16	6.98	6.98	6.98		

normal double bonding and disagrees with the conclusions above; however, such an interpretation is greatly oversimplified. Note that the basis set does not include a "3p" orbital; there are only 2p-type functions with varying degrees of diffuseness. A large part of the P p_π population comes from the core p function required to make the valence π-MO orthogonal to the formal $2p_\pi$ core. The core function is too compact (and has the wrong sign!) to contribute to π-bonding. Another contribution to the P p_π orbital comes from a diffuse p function that is used in part to describe electrons close to the oxygens and assigned in this manner by the Mulliken procedure to phosphorus. This discussion emphasizes the point that Mulliken populations are basis set populations, and basis sets are generally *not* equivalent to orthonormal atomic orbitals. This objection does not apply to the natural atomic orbital (NAO) occupancies obtained by the method of Reed and Weinhold.[17] Some NAO occupancies for PO_3^- are summarized in Table III. Note that the $3p_\pi$ occupancy is only 0.56 e. This result is graphically affirmed by the planar electron density plot of the a_2 MO, the only π-MO to which the phosphorus p_π orbitals can contribute, in Figure 2a. This plot is that of the electron density in a plane along a PO bond and perpendicular to the molecular plane. Note that, unlike the first-row all-carbon analogue trimethylenemethane, in which the central carbon p_π orbital dominates, the central phosphorus contribution in Figure 2a is rather small; the density maximum at P is less than half that at O. The ISEP value at each O in this MO is 0.49 e, or a residual p_π population on P of 0.52 e, a value close to that of the NAO population. Figure 2a shows that there is some π-bonding between P and O; the highest contour encompassing both atoms has the relatively low value of 0.019. Finally, the total π-electron projection plot (MOs, 15, 18, and 19) in Figure 2b shows further the pronounced polarization of electrons from P to O. Note that phosphorus formally contributes 2 e to these π MOs and the oxygens contribute 4. Not all of the phosphorus electrons are transferred to the oxygens; accordingly the contribution of the phosphorus p_π orbital is, as indicated above, not zero, but its contribution is relatively small.

Tris(methylene)metaphosphate Ion (2)

Six structures were optimized at the RHF level of theory using the 3-21+G* basis set within given symmetry constraints and holding the carbons and phosphorus in a single plane. The corresponding global minimum is D_3 symmetric (**2**-D_3) with a PC bond length of 1.672 Å and with the methylene groups twisted in a propeller manner by 20° with respect to the PC_3 plane (Figure 1). Reoptimization of the lowest energy structure using the larger basis sets DZ+P and DZ+Pd changes the structure but little; in particular, the PC bond lengths are essentially identical and show a good agreement with the X-ray value (1.69 Å) of the known[10] derivative of **2** (Table II). The DZ+P harmonic vibrational frequencies indicate that **2**-D_3 is a minimum (all frequencies are real). The lowest frequency, which is doubly degenerate and corresponds to twisting of the methylene groups, is fairly small (340 cm^{-1}); that is, the potential energy surface is rather flat with respect to this particular normal mode. Indeed, the D_{3h}-symmetric structure ("all-in-plane") (**2**-D_{3h}), which is a transition structure for the CH_2-twist (one imaginary frequency, i260 cm^{-1}), is only about 1 kcal mol^{-1} higher at the RHF level of theory (all three basis sets). Single-point CISD calculations using the DZ+P basis set give an energy difference ($D_{3h} - D_3$) of 1.5 kcal mol^{-1} and, after Davidson correction,[24] gives 1.9 kcal mol^{-1}, comparable to the MP2 result of 2.3 kcal mol^{-1}. The final value for this energy difference is 1.0 (CI) or 1.4 kcal mol^{-1} (MP2) after zero-point vibrational energy correction, essentially identical with that of our lowest level theoretical approach (RHF/3-21+G*). This result invites the following interpretation. If π-bonding were important in this type of compound, π and π* orbitals would have a larger energy difference in the planar D_{3h} structure than in a structure with twisted methylene groups. Accordingly, CI would be more important for the latter structure and inclusion of CI should increase the energy difference significantly. The observed result of a small effect of CI on this energy difference then suggests that π-bonding in this compound is of minor importance.

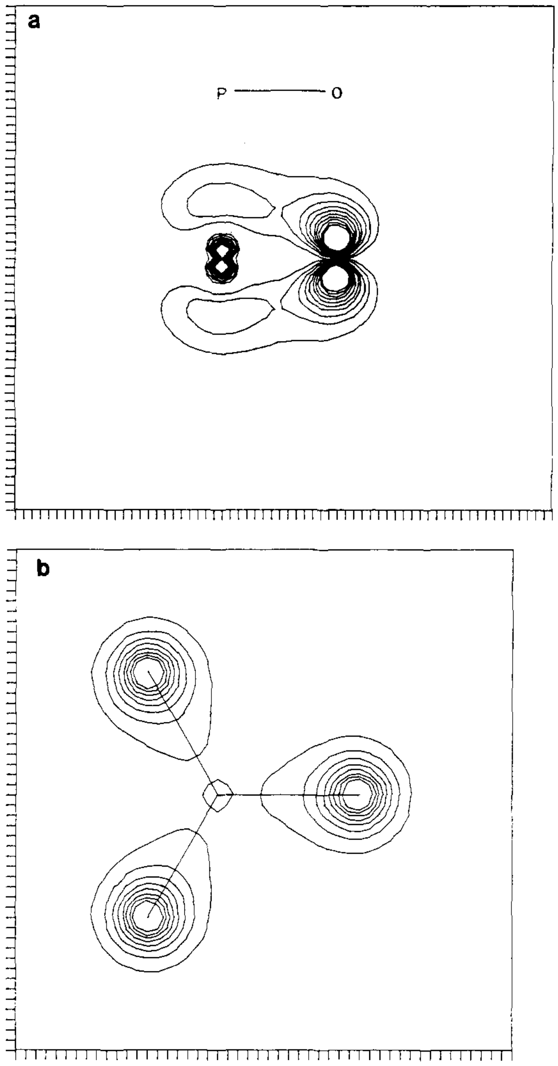

Figure 2. (a) Planar density of MO 15 of **18** 3-21+G*, for a plane containing the PO bond and perpendicular to the molecular plane. Contour levels are 0.01 to 0.1 by 0.01 e au^{-3}. (b) Projected density plot of π-MO system of **1** (MOs 15, 18, 19) for the molecular plane. Contour levels are 0.1 to 0.8 by 0.1 e au^{-2}.

The shallow bending potential for D_3 twisting of the methylene groups was confirmed by additional calculations in which the twisting angle was set at 30 and 40°. These D_3 structures have energies only 1.16 and 5.98 kcal mol^{-1}, respectively, above the global minimum and virtually unchanged PC bond lengths. This shallow potential provides further evidence that PC π-bonding is relatively weak. Although the symmetrical twisting of three methylene groups (**2**-D_{3h} → **2**-D_3) requires relatively little energy,

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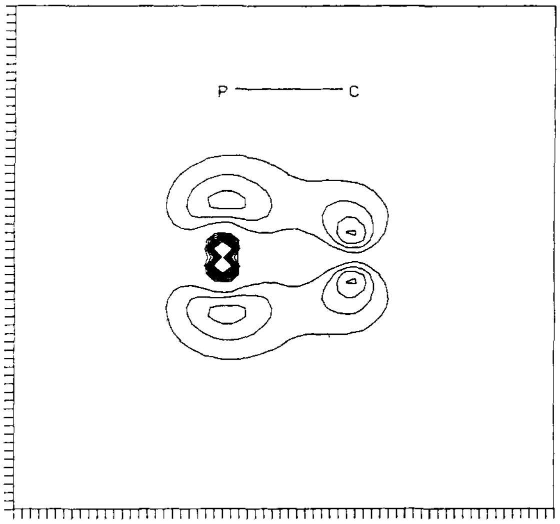

Figure 3. Planar density plot of the bonding a_2 π-MO (MO 18) for D_{3h} **2** in a plane containing a PC bond and perpendicular to the molecular plane. Contours from 0.01 to 0.1 by 0.01 e au^{-3}.

a single twist by 90° (**2**-$C_{2v}\perp$) raises the energy by 12.4 kcal mol^{-1} (Table I). The latter value may be compared with 22 kcal mol^{-1} for trimethylenemethane dianion.[9] The 90° twisting of other methylene groups is even more unfavorable energetically (**2**-$C_{2v}\perp_2$, **2**-$D_{3h}\perp_3$; Table I).

The role of PC π-bonding can be gauged qualitatively by the a_2 bonding π-MO in Figure 3 that corresponds to the analogous PO_3^- π-MO in Figure 2a. The highest contour encompassing both P and C has the value of 0.015, even less than that in **1**, undoubtedly because the bond distance is longer. Figure 3 shows charge transfer to carbon but qualitatively less than that to O in Figure 2a. **2** is too large for ISEP computation with our present programs; however, according to natural populations (NP)[17] all of the structures of **2** are highly polar. The PC bond is predominantly an ylide type with +1.7 NP formal charge at phosphorus and −1.3 at carbon (Table III). The charge at the phosphorus is approximately the same for all of the structures considered except for the triply 90° twisted ones. The third twist leads to a shift of approximately 1 e from the carbons to phosphorus (Table III). Four MO's are of interest in **2**-$D_{3h}\perp_3$: the doubly degenerate Möbius-type subjacent HOMO, the free-electron pair at P-(HOMO), and the antibonding Möbius LUMO. Thus **2**-$D_{3h}\perp_3$ can be viewed as a Möbius 4π-electron aromatic system and is 117.2 kcal mol^{-1} (DZ+P) above the planar D_{3h} structure (**2**-D_{3h}). The structure corresponding to the switched HOMO and LUMO, that is, 6π-electron antiaromatic Möbius system, is found at 131.7 kcal mol^{-1} relatively to **2**-D_{3h}. Pyramidalization at the phosphorus within the C_{3v} symmetry constraint (**2**-C_{3v}) inevitably lowers the energy of the "free electron pair at P" MO which now becomes the subjacent HOMO. The CC distances also decrease to further favor Möbius resonance. Consequently, the **2**-C_{3v} structure is about 50 kcal mol^{-1} below **1**-$D_{3h}\perp_3$ (3-21+G*, Table I). The unimportance of Möbius conjugation in **2** suggests that it is equally unimportant in **1**. Moreover, the greater electronegativity of oxygen compared to carbon makes the PO bond in PO_3^- more polar than the PC bond in **2**. This point shows up in the higher P $3p_\pi$ NAO population summarized in Table III.

The present results may be compared with recent calculations on the related neutral system bis(methylene)phosphorane, $(CH_2)_2PH$.[25] The π system was described as strongly polarized but less so than in HPO_2 (vide supra). The weakness of the π bonds was indicated by a distinct tendency toward pyramidalization around phosphorus. This interpretation, which again is based largely on Mulliken population analyses, is nevertheless consistent with our results for **2**.

Finally, we may ask why the methylene groups in **2** are twisted at all. The hydrogens on different methylene groups in planar **2** are separated by 2.9 Å, substantially outside the sum of their van der Waals radii; hence, steric effects are unlikely to be important. We suggest that the entire structure is dominated by simple Coulombic effects. The large negative charges need to stay as close as possible to the positive phosphorus but to stay mutually apart. Slight twisting moves the carbanion lobes farther apart, but additional twisting gets upper and lower lobes of two methylene groups too close. Maximum repulsion is reached at the **2**-$D_{3h}\perp_3$ structure; the close carbanion lobes in this structure account for its high energy.

Conclusion

The double-well potential energy surface of **2** with the D_3 structure as minimum and the D_{3h} structure at the top of the barrier underscores the weakness of the phosphorus–carbon $3p_\pi$–$2p_\pi$ overlap; the PC bond in **2** is ylide-like. This conclusion is confirmed by the small calculated effect of CI on the energy difference between the planar D_{3h} and twisted D_3 structures. Together with the charge distribution analysis, these results indicate dipolar structures for PO_3^- and $P(CH_2)_3^-$ in which phosphorus–oxygen and phosphorus–carbon double bonding is relatively weak and dominated by Coulombic effects.

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