assumed constant, and the values given by Schmaltz et al.[43] were used (see Table IV).

The present measurements do indeed show a new and surprising aspect of this topic: the anisotropies in the bond susceptibilities increase sharply (in absolute value) with increased halogen substitution. Another trend can be seen from the Table IV: the diamagnetic susceptibilities parallel to the C-X bond (χ_{cc}) appear to become slightly larger with increasing halogen substitution, while the perpendicular diamagnetic susceptibilities (χ_{bb}) decrease sharply; it is the latter which cause the large paramagnetic terms in the susceptibilties of the polyhalogenated methanes. A ready explanation for this is not apparent in terms of electron circulations. One possible rationale is that the perpendicular susceptibility depends on paramagnetic circulation of electrons around the chlorine nucleus via the p_x or p_y valence orbitals and the antibonding σ orbital to carbon. Additional halogen substitution could change the electron distribution and hybridization of the σ and σ^* orbitals, enhancing this circulation.

Angular Correlation. From the concentration series of chloroform and bromoform, the Kirkwood g_2 factor of the pure compounds can be calculated (eq 8). This gives $g_2(CDCl_3) = 1.07$ and $g_2(CDBr_3) = 1.13$. Battaglia and Ritchie performed an analogous concentration-dependent Cotton-Mouton study[37] in cyclohexane. Their lowest concentration is about 20 mol %. Our extrapolation of their curve leads to $g_2 = 1.20$. They themselves extrapolate differently obtaining $g_2 = 1.25$. Angular correlation has also been studied for chloroform by Alms et al.[44] using Rayleigh scattering, and for chloroform and bromoform by Patterson and Griffiths[45] from Rayleigh and Raman line-width data. Both groups report values leading to a g_2 of about 1.6 for chloroform, and the latter group finds a value of about 2.3 for bromoform, all at room temperature. These values differ substantially from those found by the NMR method or the Cotton-Mouton method. We can see two possible reasons for this discrepancy.

Firstly, it is not clear that the definition of the phenomena measured in the two kinds of studies is the same. For example, we note that a neat liquid consisting of long-lived rigid dimers with parallel major axes would yield a g_2 value of 1.0 by comparison of Rayleigh light scattering and Raman line-shape analysis, but 2.0 by the NMR method or the Cotton-Mouton effect.

The second explanation is that collision-induced changes in the effective polarizability of the small molecules studied here may perhaps not be neglected anymore. This has recently been discussed by Ladanyi et al.[46,47] who calculate that this effect will lead to an effective polarizability in Raman and Rayleigh scattering, which is lower than the molecular value. The change in α is based on a dipole-induced-dipole interaction and may be quite large in strong dipoles like the haloforms under study here. For larger polyatomic molecules these effects will become negligible,[47] so that g_2 factors of, for instance, substituted benzenes may be expected to agree better with the NMR data. Finally, in the calculation of g_2 from the ratio of Rayleigh and Raman correlation times, it is assumed that there is negligible dynamic correlation between neighbors. However, small dipolar molecules may well have a significant rotational anticorrelation, which would bring the static g_2 value into closer agreement.

The concentration-dependent study of scattering by only one technique (Rayleigh scattering) should in principle give a correct g_2 value if the viscosity of the different solutions is kept constant. Therefore the deviation between our value for $CDCl_3$ and the one obtained by Alms et al.[44] is not quite clear. Measurements on substituted benzenes performed in this way give comparable g_2 factors with the NMR technique as well as with the Cotton-Mouton effect.[6,29]

Finally it should be noted that the NMR orientation method is a clean simple technique, which provides reasonably accurate quantities to be used in a straightforward interpretable theory, where the quantities in the formulas are well known, while the optical techniques are experimentally complex and contain quantities in the formulas which are sometimes hard to obtain (local field factors, hyperpolarizability); also line-shape analyses may for many compounds be quite complex.

Scalar ^1H-^2H Couplings in the Methylene Halides. Measurements of the scalar $J_{^1H^2H}$ couplings in methylene halides were made at an early date.[48] Our measurements are more precise and lead to J_{HH} geminal coupling constants of -7.19 Hz for CH_2Cl_2, -6.41 Hz for CH_2Br_2, and -6.14 Hz for CH_2I_2.

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Registry No. C^2HCl_3, 865-49-6; C^2HBr_3, 2909-52-6; C^2HI_3, 2787-27-1; $C^2H^1HCl_2$, 1665-01-6; $C^2H^1HBr_2$, 2253-83-0; $C^2H^1HI_2$, 2253-85-2; $C^2H^1H_2Cl$, 4960-86-5; $C^2H^1H_2Br$, 1861-05-8; $C^2H^1H_2I$, 992-96-1.

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(43) Schmaltz, T. G.; Norris, C. L.; Flygare, W. H. *J. Chem. Phys.* **1973**, *59*, 7961.
(44) Alms, G. R.; Bauer, D. R.; Brauman, J. I.; Pecora, R. *J. Chem. Phys.* **1973**, *59*, 5304; **1973**, *59*, 5310.
(45) Patterson, G. D.; Griffiths, J. E. *J. Chem. Phys.* **1975**, *63*, 2406.
(46) Ladanyi, B. M. *Chem. Phys. Lett.* **1985**, *121*, 351.
(47) Ladanyi, B. M.; Levingen, N. E. *J. Chem. Phys.* **1984**, *81*, 2620.
(48) Bernstein, H. J.; Sheppard, N. *J. Chem. Phys.* **1962**, *37*, 3012.

Semipolar P-O and P-C Bonds. A Theoretical Study of Hypophosphite and Related Methylenephosphoranes

Andrew Streitwieser, Jr.,* Andrzej Rajca,[1a] Robert S. McDowell,[1b] and Rainer Glaser[1c]

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received August 25, 1986*

Abstract: Structures, energies, and electronic structures as derived from integrated projected densities are presented from ab initio MO calculations of H_3PO (**1**), H_3PCH_2 (**2**), $H_2PO_2^-$ (**3**), $OPH_2CH_2^-$ (**4**), and $H_2P(CH_2)_2^-$ (**5**). The results show that allylic conjugation is not important in **3**, **4**, and **5** and that the PO and PC bonds in these compounds are best represented as dipolar bonds with little double-bond character. Simple electrostatic considerations suffice to interpret many of the results obtained concerning structure and energy.

The nature of the phosphorus-oxygen bond in phosphine oxides[2-6] and of the phosphorus-carbon bond in ylides[7-10] has received much recent theoretical attention. Hartree-Fock calculations together with structural effects, population analyses, and analyses

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of molecular orbitals and their involvement with d orbitals has led to a general picture of predominant semipolar bonding with a small degree of back-bonding; that is, multiple bonding to phosphorus in these compounds is small and d orbitals play only a minor role.[11] On the other hand, a recent general valence bond (GVB) description appears to emphasize such multiple bonding and ascribes a larger bonding role to d orbitals.[8] In the present study we compare phosphine oxide, H_3PO (**1**), and methylenephosphorane, H_3PCH_2 (**2**), with the related anions that incorporate two such PO and PC bonds: phosphinate (hypophosphite) ion, $H_2PO_2^-$ (**3**); methylenephosphoranyloxide ion, $CH_2PH_2O^-$ (**4**); and methylenephosphoranylmethyl anion, $H_2P(CH_2)_2^-$ (**5**). In addition to structural effects, the study includes approximate integrated spatial electron populations[12] of significant regions.

Calculations

Older calculations were accomplished with GAMESS[13] and more recent calculations used GAUSSIAN-82.[14] The standard 3-21G* basis set[15] was used with the standard P d-exponent of 0.55.[16] Some older calculations made use of a preliminary P d-exponent of 0.47; the use of this exponent is denoted by a prime on the basis set, e.g., 3-21G*′. Note that the optimized d-exponent for **1** with the 3-21G* basis set is 0.523.[5b] Calculations of ions included diffuse orbitals (denoted as 3-21+G*, etc.) as prescribed by Schleyer et al.[17] A few calculations were done with the double-ζ basis set of Dunning and Hay[18] with polarization functions on all centers and denoted DZ+P. Harmonic vibrational frequencies were calculated analytically.[19]

Projected electron density functions were calculated using PROJ[20] and the numerical "integrated spatial electron populations", ISEP, integrations were carried out for regions bounded by minima in the projected density functions.[21] The minimum density demarcations of such projected functions are approximations to the virial boundaries of Bader;[22] these boundaries are vertical curtains compared to the true virial curved surfaces. Accordingly, the derived integrated populations are only approximations to the true integrations over Bader "basins"; however, they are expected to be qualitatively correct and are faster to compute.

Table I. Optimized Geometries of Methylenephosphorane (**2**)

	3-21G	3-21G*′	3-21+G*′
bond lengths, Å			
P–C	1.728	1.666	1.677
P–H′	1.437	1.424	1.419
P–H″	1.404	1.395	1.393
P–H″	1.404	1.395	1.393
C–H	1.072	1.077	1.079
bond angles, deg			
H′–P–C	128.7	128.7	128.2
H–C–H	119.8	117.4	117.5
β^a	25.4	24.5	24.2
dipole moment, D	2.71	2.34	2.90
ISEP (CH_2) e	8.858[b]	9.165	
-*E*, hartrees	379.3986	379.5667	379.5769

[a] Angle between HCH plane and PC bond. [b] 9.003 at 3-21G(*′).

Results and Discussion

H_3PO (1) and H_3PCH_2 (2). These compounds have been much studied theoretically at a variety of basis-set levels. Basis-set effects on the geometry and integrated charge distribution of **1** have been summarized recently.[23] Basis sets of at least split valence shell quality with d orbitals on all heavy centers give a consistent structure with a PO bond length of about 1.47 Å and an integrated oxygen charge of −1.53 to −1.58. The large negative charge on oxygen suggests that the dipolar structure $H_3P^+{-}O^-$ dominates in phosphine oxide and that the "double-bond" structure $H_3P{=}O$, which involves charge transfer from anion to cation, contributes but little.

The same type of approach may be applied to methylenephosphorane (**2**). Here also a number of calculations of at least split valence shell quality with d orbitals on phosphorus give consistent structures with PC distances of 1.65–1.67 Å.[7,24-28] The optimized structure has C_s symmetry with a nonplanar CH_2 group bent up and eclipsing one P–H,[27,28] but the inversion barrier is low. The integrated population for the CH_2 group is 9.165 e (3-21G*′ basis)[28] for a net charge of −1.165. It was not possible to dissect this charge between C and H; hence, it refers to the methylene group as a unit. The charge is less than for O in H_3PO as expected for the lower electronegativity difference between P and CH_2 but the magnitude is still rather high and indicates that the ylide structure $H_3P^+{-}CH_2^-$ dominates the methylenephosphorane structure $H_3P{=}CH_2$.[29]

There have been many discussions of the role of d orbitals in the stabilization of the ylide PC bond. An interesting contribution to these discussions involves the effect of basis set on the CH_2 ISEP charge. The 3-21G optimized structure, without any d orbitals, has a long PC bond. With d orbitals only on phosphorus (3-21G(*′) basis), the PC bond is shortened substantially. Putting d orbitals on carbon as well (3-21G*′ basis) has only a slight additional effect (Table I). Note, as indicated above, that the phosphorus d orbitals in these bases have an exponent of 0.47 rather than the 0.55 standard for 3-21G*. Table I also summarizes the effect of basis set on the ISEP charge on the CH_2 group in **2**; note that as d orbitals are added successively to P and then to

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[1] (a) Miller Institute Fellow, 1985–87. (b) Eastman Kodak Fellow, 1983–85. (c) Fonds Stipendiat des Verbandes der Chemischen Industrie, 1985–87.

[2] Wallmeier, H.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1979**, *101*, 2804–2814.

[3] Schmidt, M. W.; Yabushita, S.; Gordon, M. S. *J. Phys. Chem.* **1984**, *88*, 382–389.

[4] Gordon, M. S.; Boatz, J. A.; Schmidt, M. W. *J. Phys. Chem.* **1984**, *88*, 2998–3002.

[5] (a) Schmidt, M. W.; Gordon, M. S. *Can. J. Chem.* **1985**, *63*, 1609–1615. (b) Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 1922–1930.

[6] Bollinger, J. C.; Houriet, R.; Kern, C. W.; Perret, D.; Weber, J.; Yvernault, T. *J. Am. Chem. Soc.* **1985**, *107*, 5352–5358.

[7] Eades, R. A.; Gassman, P. G.; Dixon, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 1066–1068.

[8] Dixon, D. A.; Dunning, T. H., Jr.; Eades, R. A.; Gassman, P. G. *J. Am. Chem. Soc.* **1983**, *105*, 7011–7017.

[9] Vincent, M. A.; Schaefer, H. F., III; Schier, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1983**, *105*, 3806–3811.

[10] Schoeller, W. W.; Niemann, J. *J. Am. Chem. Soc.* **1986**, *108*, 22–26.

[11] Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272–295.

[12] For some examples see: Collins, J. B.; Streitwieser, A., Jr. *J. Comput. Chem.* **1980**, *1*, 81; Streitwieser, A., Jr.; Grier, D. L.; Kohler, B. A. B.; Vorpagel, E. R.; Schriver, G. W. *Electron Distributions and the Chemical Bond*; Coppens, P., Hall, M., Eds.; Plenum Press: New York, 1982. Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 5818–24. McDowell, R. S.; Streitwieser, A., Jr. *Ibid.* **1985**, *107*, 5849–55.

[13] Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC No. QG01.

[14] Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon University, Pittsburg, PA.

[15] Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039–5048.

[16] Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654–3665.

[17] Clark, T.; Chandrasekhar, J.; Spitznagel, G.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

[18] Dunning, T.; Hay, P. In *Methods of Electronic Structure Theory*; Schaefer, H. J., III, Ed.; Plenum Press: New York, 1977; p 1. Dunning, T. *J. Chem. Phys.* **1970**, *53*, 2823.

[19] Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1979**, *S13*, 225.

[20] Collins, J. B.; Streitwieser, A., Jr.; McKelvey, J. *Comput. Chem.* **1979**, *3*, 79.

[21] McDowell, R. S.; Grier, D. L.; Streitwieser, A., Jr. *Comput. Chem.* **1985**, *9*, 165–9.

[22] Bader, R. F. W. *Acc. Chem. Res.* **1975**, *8*, 34–40; **1985**, *18*, 9–15. Bader, R. F. W.; MacDougall, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 6788–95. Biegler-Koenig, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317–28. The significance of integrated populations over Bader "basins" has been discussed recently by: Slee, T. S. *J. Am. Chem. Soc.* **1986**, *108*, 7541–8.

[23] Streitwieser, A.; Jr.; McDowell, R. S.; Glaser, R. *J. Comput. Chem.*, in press.

[24] Lischka, H. *J. Am. Chem. Soc.* **1977**, *99*, 353–60.

[25] Strich, A. *Nouv. J. Chim.* **1979**, *3*, 105–8.

[26] Trinquier, G.; Malrieu, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 7169–72.

[27] Mitchell, D. J.; Wolfe, S.; Schlegel, H. B. *Can. J. Chem.* **1981**, *59*, 3280–92.

[28] McDowell, R. S.; Streitwieser, A., Jr. *J. Mol. Struct.* (*THEOCHEM*) **1986**, *138*, 89–95.

[29] Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907–927.

Table II. Harmonic Vibrational Frequencies Calculated for **4A** at the RHF/3-21+G* Level

normal mode, C_s	freq, cm^{-1}	normal mode, C_s	freq, cm^{-1}
A″	253.4	A′	1217.1
A′	391.3	A′	1246.3
A′	610.6	A′	1548.6
A″	659.8	A″	2531.9
A′	917.9	A′	2566.9
A″	1038.6	A′	3196.1
A″	1164.3	A″	3250.9
A′	1205.5		

Table III. Structure, Energies, and ISEP of H_3PO (**1**), $H_2PO_2^-$ (**3**), and $OPH_2CH_2^-$ (**4**)

	1[a]	**3**[b]	**4**[b]
r(PH), Å	1.400	1.418	
r(PO), Å	1.467	1.505	1.518
Δr(PO), Å[c]		0.024	
r(PC), Å			1.726
Δr(PC), Å[c]			0.049
ISEP (O), e	9.535[d]	9.603 9.589[e]	9.624 9.636[e]
ISEP (CH_2), e			9.394 9.323[e]
$-E$, hartrees	415.28498	489.32592 489.33805[e]	453.57283 453.58344[e]

[a] 3-21G*′ [b] 3-21+G*′ [c] Relative to neutral parent with the 3-21+G*′ basis. [d] 9.562 e at 3-21G*′; 9.527 e at 3-21G*. [e] 3-21+G*.

C as well, the ISEP charge on the CH_2 group *increases*. The d orbitals, particularly on phosphorus, are clearly required for effective polarization stabilization of the anionic charge. Such polarization stabilization does not involve charge transfer.

That is, the primary role of phosphorus d-functions in phosphonium ylides is *polarization* of electron density around phosphorus away from the carbanionic charge and of the carbanion electrons toward the positively charged phosphorus, thereby achieving better Coulombic stabilization. The electrostatic energy of interaction between a charge and the induced dipole of a polarizable center varies as the fourth power of their distance of separation. That is, stabilization by polarization has a high distance dependence; hence, effective stabilization of the carbanion by phosphorus requires a PC distance as short as possible. In effect, d orbitals or comparable "polarization functions" in the basis set allow the computational implementation of higher order electrostatic interactions. Such polarization functions are required for adequate description of electrostatic interactions as much as for overlap effects. In the absence of d orbitals the only other important mechanism for charge stabilization apparently involves some charge transfer, perhaps via π-type bonding with an orbital that has significant antibonding character between phosphorus and the remaining ligands.[30]

Phosphinate Ion, $H_2PO_2^-$ (3). Another approach to determining the relative roles of dipolar and multiple bonding in phosphine oxide and ylide-type compounds is to compare structures with *two* oxide and methylene groups on phosphorus. The point here is to evaluate the role of allylic-type resonance, as in **3a** and **3b**, compared with the analogous dipolar structure, **3c**, in a compound such as phosphinate (hypophosphite) ion:

$$\underset{\textbf{3a}}{^-O{-}PH_2{=}O} \qquad \underset{\textbf{3b}}{O{=}PH_2{-}O^-} \qquad \underset{\textbf{3c}}{^-O{-}PH_2^+{-}O^-}$$

If allylic conjugation of the **3a**,**b** type is important, the PO bond length and the effective charge on oxygen would be expected to increase significantly; however, if the dipolar structure best represents the PO bond, then little change is expected.

There have been several recent ab initio theoretical studies of phosphinic (hypophosphorous) acid, $H_2PO(OH)$,[4,5b,31] but there are apparently no such prior studies of its anion, $H_2PO_2^-$. There do exist several semiempirical studies of the acid and the anion.[32] The optimized structure at the 3-21+G*′ level has C_{2v} symmetry with a OPO bond angle of 122.6° and a PO bond length of 1.505 Å, only 0.02 Å longer than the PO bond in H_3PO optimized with the same basis set[23] (note the inclusion of diffuse orbitals in the 3-21+G*′ basis set). The P–H bond length of 1.418 Å is also 0.02 Å longer than that in H_3PO. Thus, the structure of the anion does not suggest a significant contribution from allyl-type resonance. The ISEP of oxygen in **3** is 9.603, only 0,04 e greater than the value 9.562 obtained for **1** with the same basis set.[23] These results suggest that **3c** is the best simple representation of $H_2PO_2^-$.

Methylenephosphoranyloxide Ion, $CH_2PH_2O^-$ (4). Methylenehydroxyphosphorane, $HOPH_2CH_2$, is the hypothetical tautomer of methylphosphine oxide. **4** is the conjugate anion of these tautomers and apparently has not previously been treated theoretically. The 3-21+G*′ optimized structure **4A**, has C_s symmetry with a pyramidal methylene group bent up toward the oxygen. This structure is a local minimum with no imaginary frequencies; calculated vibration frequencies are summarized in Table II. The PO bond length, 1.518 Å, is 0.01 Å longer than that in **3** and 0.024 Å longer than that in **1**. The PC bond length, 1.726 Å, is 0.049 Å longer than that in **2** using the same basis. The O–P–C bond angle is 127.6°. ISEPs summarized in Table III show that the oxygen is slightly more negative, by 0.02 e, than in **3**, but the CH_2 group is significantly more negative, by 0.19 e, than is **2** with the same basis set,

Neither the bond length changes nor the changes in charge distribution suggest any important role for allylic-type conjugation in this system. Although the high magnitudes of the integrated charges do point unambiguously to highly dipolar bonding in these ions, this use of such charges is still controversial, in part because the integrated charges based on the total electron density of the molecule differ frequently from the charge distributions given by Mulliken populations,[33] However, in the present case, the replacement of an oxygen in phosphinate ion by a methylene group provides an additional *structural* criterion for electronic structure. Note that the HCH plane in **4A** is perpendicular to the OPC plane. If allylic conjugation were important, we would expect the CH_2 group to lie in the OPC plane in order to maximize π conjugation. In fact, such a structure, **4B**, is 5.35 kcal mol^{-1} above the global minimum (3-21+G*). The minimum energy structure of **4** has a pyramidal methylene group with the carbanionic lone pair directed away from then negative oxygen.

Methylenephosphoranylmethyl Anion, $H_2P(CH_2)_2^-$ (5). This anion is the conjugate base of methylphosphine ylide. It has long been known that alkylidenetrialkylphosphoranes are readily metalated;[34] many organometallic derivatives are now known in which the two methylene groups are bound to the same metal or to separate metals.[29,35] The structure of **5** is particularly important in the context of the present paper because the stereochemical relationship of the two methylene groups with respect to each other provides a further structural criterion for the extent of through-conjugation involving the phorphorus; that is, resonance of the type **5a** ↔ **5b** implies a p_π interaction between the CH_2's as part

$$\underset{\textbf{5a}}{^-CH_2{-}PH_2{=}CH_2} \qquad \underset{\textbf{5b}}{CH_2{=}PH_2{-}CH_2^-}$$

$$\underset{\textbf{5c}}{^-CH_2{-}PH_2^+{-}CH_2^-}$$

of the same π-type MO. The two CH_2 groups should then share a common symmetry plane, a structural feature not meaningful for the phosphinate ion. On the other hand, the dipolar structure **5c** has no such symmetry requirement for the methylene groups.

Seven structures for **5** were optimized at the RHF/3-21+G* level of theory within certain constraints of structure and symmetry. Selected geometrical parameters and energies are collected

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(30) Whangbo, M.-H.; Wolfe, S. *Can. J. Chem.* **1976**, *54*, 949–962.

(31) Ewig, C. S.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 1965–71.

(32) Bakirov, M. N.; Vakhidov, R. S.; Landau, M. A. *Dvoinoi Sloi Adsorbtsiya Tverd. Elektrodakh* **1978**, *5*, 26–9. Bakirov, M. N.; Vakhidov, R. S. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1981**, *24*, 1504–7.

(33) Bachrach, S. M.; Streitwieser, A., Jr., to be published.

(34) Wittig, G.; Polster, R. *Justus Liebigs Ann. Chem.* **1956**, *599*, 1.

(35) Kaska, W. *Coord. Chem. Rev.* **1983**, *48*, 1–58.

Table IV. Optimized Geometries and Energies for $CH_2PH_2CH_2$ Anions at 3-21+G*[a]

	r(PC), Å	∠(CPC), deg	dihedral angles, deg HCPX[a] or HPCH				$-E$, hartrees	ΔE, kcal mol^{-1}
5A C_{2v}	1.705	116.3	0.0,	180.0,	0.0,	180.0	417.82309	3.46
5B C_s	1.707, 1.713	121.9	0.0,	180.0,	90.0,	−90.0	417.82335	3.30
5C C_{2v}	1.716	132.3	90.0,	−90.0,	90.0,	−90.0	417.81944	5.75
5D C_s	1.717	116.5	−16.8,	16.8,	16.8,	−16.8	417.82347	3.23
5E C_2	1.723	116.3	−21.1,	21.1,	−21.1,	21.1	417.82438	2.66
5F C_{2v}	1.745	134.0	64.3,	−64.3,	−64.3,	64.3	417.82861	0.00
5G C_s	1.709, 1.743	123.6	60.0,	180.0,	−63.7,	63.7	417.82773	0.55

[a] Dihedral angle between PX or PC and all four CH; X is a dummy atom such that PX is the bisector of the CPC angle.

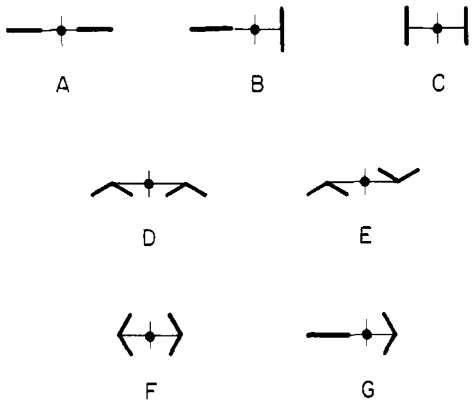

Figure 1. Schematic structures of **5**. The heavy lines indicate the planar or pyramidal orientations of the methylene groups viewed head-on with the PH_2 group perpendicular and in the center.

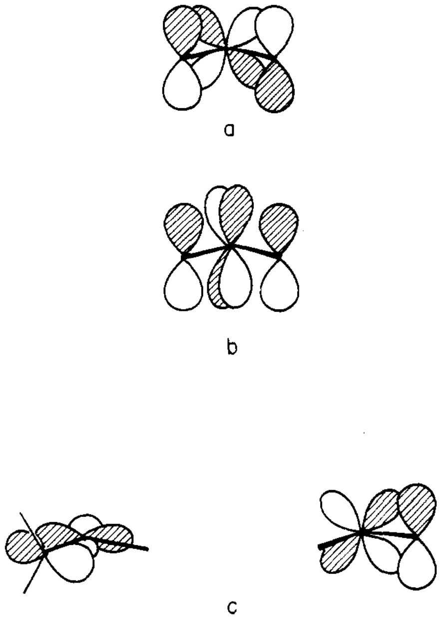

Figure 2. Interactions of carbon 2p orbitals with a central phosphorus d orbital: (a) antisymmetric π-MO; (b) symmetric π-MO, (c) the carbon 2p orbitals are perpendicular and interact with different d orbitals.

in Table IV and the structures are represented schematically in Figure 1. The first structure to be considered is the C_{2v}-symmetric structure **5A** in which both CH_2 groups and the P are in the same plane. If through-conjugation involving a d orbital on phosphorus is important, this structure should be favored because the antisymmetric combination of carbon $2p_z$ orbitals can best interact with a d orbital as shown in Figure 2a. However, the interaction of an orthogonal d orbital with the symmetric combination of carbon 2p orbitals shown in Figure 2b is approximately equally important. Dewar had pointed out years ago that such a case is equivalent to two localized dπ–pπ bonds for which through-conjugation gives no additional stabilization.[36] Rotation of one methylene group through 90° gives structure **5B**. Interaction of the dπ–pπ type in this structure involves two orthogonal p orbitals as shown in Figure 2c. However, these interactions are exactly equivalent (except for molecular symmetry differences) to the combined interactions in Figure 2a,b. That is, if the individual dπ–pπ interactions are approximately the same, as in the present case, there is no d-orbital contribution to the rotation barrier around a P–CH_2 bond. The energy difference between **5A** and **5B** is, in fact, only 0.16 kcal mol^{-1}.

A third structure involving planar methylene groups is obtained by rotating both CH_2's in **5A** by 90°. The resulting structure, **5C**, has the highest energy of all, 2.29 kcal mol^{-1} higher than **5A**. In this structure the two filled carbon 2p orbitals are pointing toward each other; this feature suggests that simple Coulombic effects of carbanion-like moieties dominate the energetics. This view is reinforced by effects of pyramidalization of the methylene groups. The remaining four structures contain pyramidal methylene groups and all are more stable than the foregoing structures with planar methylenes.

Starting with **5A**, pyramidalization in the same sense gives the C_s structure **5D**, and pyramidalization in the opposite sense gives the C_2 structure **5E**. These structures have longer CP bonds than those with planar methylenes. The most stable structure was obtained by starting with the structure of highest energy, **5C**, and pyramidalizing with the carbanionic lone pairs pointing away from each other, "exo–exo", giving structure **5F**. This structure was also obtained by starting with an "exo–endo" geometry and optimizing with the C_s symmetry constraint. Additional single-point calculations on the "exo–endo" and "endo–endo" structures obtained from **5F** by "reversing" the CH_2 pyramidalization gave energies of 6.29 and 14.40 kcal mol^{-1}, respectively, relative to **5F**. Because the potential energy surface is rather flat, we cannot exclude definitely a local minimum corresponding to an "exo–endo" structure.

Starting with **5B** and allowing the perpendicular methylene to pyramidalize while retaining C_s symmetry gives the structure **5G**, which is only 0.55 kcal mol^{-1} less stable than **5F**. Allowing both methylenes to pyramidalize would give a structure with no symmetry. The global minimum structure may indeed be of C_1 symmetry but the results above suggest that **5F** cannot be much higher in energy than the global minimum.

Of additional interest is the wide variation found for the CPC angle in these various conformations. The range of 116–134° suggests that the groups are rather flexible around the phosphorus. The computed structures may be compared with the crystal structure reported recently for a closely related lithium compound. The compound $(C_6H_5)_2P(CH_2)_2Li$ is a dimer with two lithiums bridging the methylenes of two phosphorus units in an eight-membered ring.[37] The P–CH_2 bond distances of 1.71 Å are close to those found for many of the conformations of **5**. Moreover, the methylene groups are pyramidal and the CPC bond angle of 114° is close to the range found for **5**, particularly considering the expected effect of the two phenyl groups bound to phosphorus in the crystal structure compared to the PH_2 group in **5**. Crystal structures are now available for derivatives of **5** with alkyl or phenyl groups replacing the hydrogens on phosphorus and with

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(36) Dewar, M. J. S. *Rev. Mod. Phys.* **1963**, *35*, 586–598. Dewar, M. J. S; Lucken, E. A. C.; Whitehead, M. A. *J. Chem. Soc.* **1960**, 2423–9.

(37) Cramer, R. E.; Bruck, M. A.; Gilje, J. W. *Organometallics* **1986**, *5*, 1496–9.

Table V. Integrated Spatial Electron Populations (ISEP) about CH_2, Minimum Value of the Projection Function along the PC Bonds in $CH_2PH_2CH_2$ Anions at 3-21+G*, and Formal Charges of CH_2 and PH_2 Groups

	ISEP (CH_2), e	P_{min}, e au^{-2}	net charge PH_2	net charge CH_2
5A	9.395	0.478	+1.79	-1.40
5B coplanar	9.411	0.484	+1.75	-1.41
5B perpend	9.337	0.436		-1.34
5C	9.317	0.442	+1.63	-1.32
5D	9.356	0.475	+1.71	-1.36
5E	9.328	0.473	+1.66	-1.33
5F	9.260	0.441	+1.52	-1.26

the methylene groups bound to a wide range of metals throughout the periodic table. Most of these structures have P–CH_2 bond distances in the range 1.76 ± 0.03 Å and CPC bond angles of 112–116° (although some bond angles are as low as 97–102°); all have pyramidal methylene groups.[38] All of these compounds have rings incorporating one or more phosphorus units and one or more metals; hence, the appropriate structures of **5** to consider for comparison are closer to **D** and **E** than to the lowest energy structure **F**. The flexibility of these organometallic structures and their relationship to **5** suggests that the carbon–metal bonding in these compounds has high ionic character.

Integrated spatial electron populations (ISEP) indicate polar PC bonds for all of the structures of **5**. The pyramidal methylene groups have longer PC bonds than the planar methylenes but also have less group charge. For example, the ISEP of the methylenes in the most stable structure **5F** is only 0.12 e greater than that of the methylene in **2** (calculated with the same basis set), a remarkably small difference considering that **2** is neutral and **5** is an anion. Moreover, the methylene ISEP in **5F** is *less* than that in **4**. If any type of resonance conjugation were important in these compounds the electronegative oxygen of **4** would certainly be expected to absorb more charge than carbon. *The inescapable conclusion is that both groups are essentially fully anionic and that conjugation is unimportant.*[39]

Some of the structural and charge changes can be rationalized. The reduced ISEP of pyramidal methylenes may result from more effective σ donation to phosphorus. With less total charge and with the carbanionic lone pair already effectively farther from the phosphorus, the effectiveness of polarization is reduced and a short PC distance is less important. The higher charge of planar methylene groups requires more polarization stabilization and a shorter PC distance. This is not the only effect, however, since the ISEP of planar methylene groups depends on the orientation relative to the HPH plane; simple rotation of planar methylenes from coplanarity with the CPC plane (perpendicular to HPH) to perpendicular to the CPC plane causes a substantial reduction in the net charge on the CH_2 group, about half the effect of pyramidalization (Table V). Thus, interaction with PH_2 fragment orbitals is not insignificant. It may be significant to note how well this classical electrostatics argument applies to the organometallic derivatives of **5**. When the methylene groups are also close to a large and polarizable metal cation, the polarizability of phosphorus is less important for stabilization of the carbanion and the PC bond distances tend to be longer; the PC bond distance in the lithium salt is shorter than those in the other derivatives (vide supra).

The sharp distance requirement for polarization also provides an explanation for the generally shorter bonds between phosphorus and negatively charged atoms compared to comparable bonds to neutral atoms (e.g., PO^- vs. POH, PCH_2^- vs. PCH_3, etc.). That is, many of these structural effects can be interpreted with simple electrostatic considerations; double bonding is not required to explain these bond-length changes. Finally, consider the disproportionation equilibrium:

$$\underset{\mathbf{3}}{H_2PO_2^-} + \underset{\mathbf{5F}}{H_2P(CH_2)_2^-} = \underset{\mathbf{4A}}{2OPH_2CH_2^-}$$

$$\Delta E = -0.13 \text{ kcal mol}^{-1} \quad (3\text{-}21\text{+G*})$$

This is an isodesmic reaction in which all components have the same charge. The computed result of virtual thermoneutrality for this reaction should therefore not be far in error. This result also indicates that the PO and PCH_2 groups are essentially independent entities in these systems with little differential mutual interaction. Finally, although the present study is only at the Hartree–Fock level, the small effects of extensive CI on relative energies of the related trimethylenemetaphosphate ion[40] suggests that such CI would not change the results significantly.

We conclude that hypervalent phosphorus is a poor mediator of allylic resonance. The phosphorus–carbon and phosphorus–oxygen bonds in ylide and phosphine oxide type compounds is predominantly polar, and the best simple electronic representation of these compounds is as dipolar structures. Simple electrostatic interactions suffice to interpret many of these structures and relative energies without recourse to unusual bonding modes.

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Supplementary Material Available: Appendix of optimized geometries for **3**, **4A**,**B**, and **5A–G** (4 pages). Ordering information is given on any current masthead page.

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(38) Many structures are summarized in ref 29 and 35.

(39) The ionic structure is also consistent with bond distances in a uranium derivative: Cramer, R. E.; Mori, A. I.; Maynard, R. B.; Gilje, J. W.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1984**, *106*, 5920–6.

(40) Rajca, A.; Rice, J. E.; Streitwieser, A., Jr.; Schaefer, H. F., III *J. Am. Chem. Soc.*, following paper in this issue.