

Characterization of NMR Shielding in 7-Phosphanorbornenes

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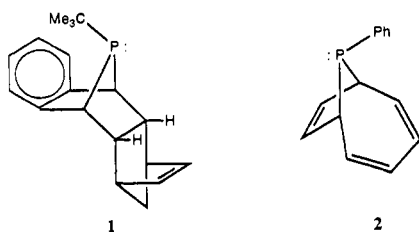
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Abstract: Ab initio chemical shielding calculations employing the gauge-including atomic orbital (GIAO) method have been carried out on a series of phosphorus bicyclic and monocyclic molecules in order to provide an understanding of the unusual chemical shifts seen in 7-phosphanorbornene compounds. It is shown that the strong interaction between the phosphorus substituent (hydrogen, in the models studied here) and the carbon–carbon double bond is responsible for the large deshielding seen in these systems. The localized nature of the phosphorus lone pair, the carbon–carbon double bond, a phosphorus p orbital perpendicular to the molecular C_v plane of symmetry, and their energy proximity to the HOMO–LUMO energy gap give rise to large calculated deshieldings in good agreement with experimental trends. Model calculations on the monocyclic systems as a function of flap angle correlate well with results from the bicyclic molecules, and it is shown that the calculated shieldings in the present study relate in a simple way to the HOMO–LUMO energy gap.

Introduction

Phosphorus-31 NMR shifts cover a very wide range (1415 ppm^{1a}) and even for similar phosphorus functionalities can exhibit pronounced sensitivity to molecular structural modification. These shift effects are of great empirical value but in many cases are not well understood and lack a theoretical basis. Nowhere are the effects of structure on shifts so pronounced as in the family of bridged unsaturated phosphines, where angle and rotational constraints can be strong and atoms can be held in fixed positions that might allow specific orbital interactions to develop. Indeed, one such cyclic phosphine has the most *downfield* shift ever recorded for any tertiary phosphine with a shielding² of 175.9 ppm (1, $\delta +152.5^3$) while another (2, 407 ppm ($\delta -79^4$)) shows such strong *shielding* that it is well beyond that of any noncyclic tertiary phosphine. A satisfactory theoretical description that accounts for such enormous effects has never been developed.



Substantial progress has been made in recent years on the calculation of the ³¹P NMR shift of simple molecules,^{5–8} but

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(1) Tebby, J. C. *Handbook of Phosphorus-31 Nuclear Magnetic Resonance*; CRC Press: Boca Raton, FL, 1991; (a) p 8; (b) p 134.

(2) Chemical shieldings reported in this paper are given in parts per million (ppm) on an absolute basis as are the values which are calculated theoretically. They may readily be converted to chemical shifts relative to 85% phosphoric acid (shown in parentheses as $\delta+$ or $\delta-$ values) by using the absolute shielding for this species, which is found to be 328.4 (Jameson, C. J.; de Dios, A. C.; Jameson, A. K. *Chem. Phys. Lett.* **1990**, *167*, 575). Experimental shifts, likewise, were converted to absolute shieldings using the absolute shielding for phosphoric acid. See the discussion under Computational Details.

(3) Quin, L. D.; Bernhardt, F. C. *J. Org. Chem.* **1986**, *51*, 3235.

(4) Katz, T. J.; Nicholson, C. R.; Reilly, C. A. *J. Am. Chem. Soc.* **1966**, *88*, 3832.

(5) Bouman, T. D.; Hansen, A. E. *Chem. Phys. Lett.* **1990**, *175*, 292.

there has been no attempt to study the effect of changes in the carbon framework on the shifts of a particular type of phosphorus functional group. With the aid of the more advanced computing platforms, it is now possible to calculate ³¹P NMR shifts for molecules approaching the size where large structural influences on shielding can be seen experimentally. The family of 7-phosphanorbornenes is an excellent case in point. Because of the configurational stability of phosphorus, *syn* and *anti* isomers are possible for this structural type. There is exceptionally strong deshielding in derivatives of both of the isomeric forms, but it is especially pronounced in those with the *syn* structure.⁹ The molecular size (C₆H₉P when unsubstituted) is of a magnitude that meaningful ab initio calculations can now be performed to help understand the origin of these shielding effects. In this paper, we present the results of such calculations and are able to derive an interpretation of the effects in terms of basic facets of the theory.

Experimental Background

The 7-phosphanorbornene ring system is easily constructed by reaction of Diels–Alder dienophiles with phosphole oxides, as well as by the related dimerization of these compounds.¹⁰ Early attempts to prepare phosphines in this series by deoxygenation of the phosphine oxides were unsuccessful, and it was not until 1980¹¹ that this was first accomplished. As shown in Scheme I, the Diels–Alder reactions are specific in giving oxides with the singly bonded substituent in the *syn* position relative to the C=C unit, and this structure is retained in the deoxygenation process that gives the phosphine.⁹

A technique was also devised¹² that caused inversion of the configuration of the phosphine and was useful in providing samples of the *anti* isomer (Scheme II). Both isomers have sufficient thermal stability to permit easy chemical characterization. Especially intriguing was the observation of the ³¹P NMR properties of these phosphines,⁹ both isomers gave shifts

(6) Chesnut, D. B.; Rusiloski, B. E. *Chem. Phys.* **1991**, *157*, 105.

(7) Chesnut, D. B.; Rusiloski, B. E. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkade, J. G., Eds.; VCH Publishers: Deerfield Beach, FL, in press.

(8) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Basic Principles and Progress*; Diehl, P.; Fluck, E., Günther, H., Kosfeld, R., Seelig, J., Eds.; Springer: Berlin, 1990; Vol. 23, p 165.

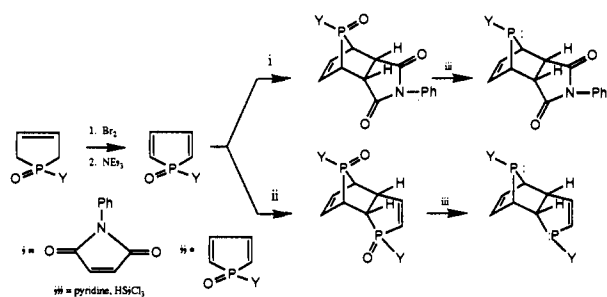
(9) Quin, L. D.; Caster, K. C.; Kivalus, J. C.; Mesch, K. A. *J. Am. Chem. Soc.* **1984**, *106*, 7021.

(10) These and other reactions leading to 7-phosphanorbornenes have been recently discussed: Quin, L. D. *Rev. Heteroat. Chem.* **1990**, *3*, 39.

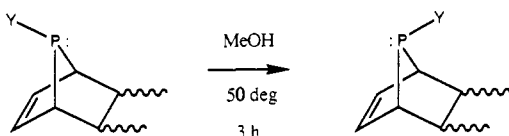
(11) Quin, L. D.; Mesch, K. A. *J. Chem. Soc., Chem. Commun.* **1980**, 959.

(12) Mesch, K. A.; Quin, L. D. *Tetrahedron Lett.* **1980**, *21*, 4791.

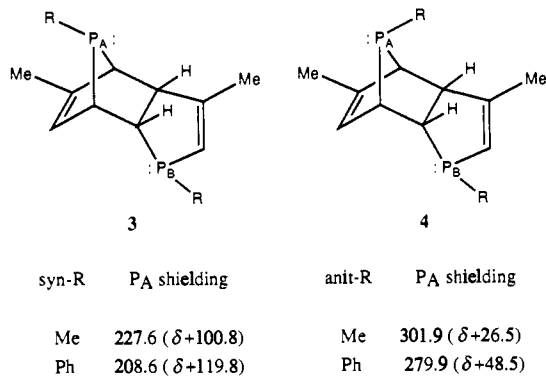
Scheme I



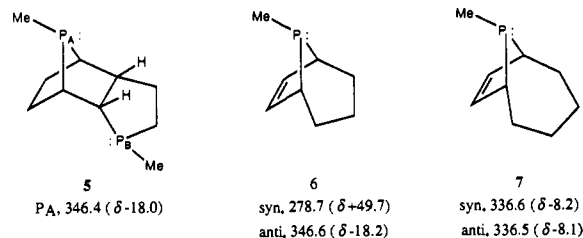
Scheme II



that reflected exceptionally strong deshielding, but this was much more pronounced with the *syn* isomer (by some 60–70 ppm relative to the *anti* isomer). Signals for many of the *syn* isomers occurs in the 180–230 ppm shielding range ($\delta +150$ to $\delta +100$) with the record being set at 175.9 ppm ($\delta +152.5$) by the benzo derivative **1**.³ Structures **3** and **4** are illustrative of this *syn*, *anti* effect. To place these shifts in context, it should be remembered that the great majority of tertiary phosphines have *negative* chemical shifts with respect to phosphoric acid; at the time of the discovery of the phosphanorbornenes, the most deshielded tertiary phosphine known was the tri-*tert*-butyl derivative, with shieldings of from 265 to 267 ppm ($\delta +63$ to $\delta +61$).^{1b} The contracted bond angle (79° ¹⁰) in the 7-phosphanorbornenes is clearly not alone the cause of the strong deshielding; in the corresponding saturated structure (as in **5**) the angle



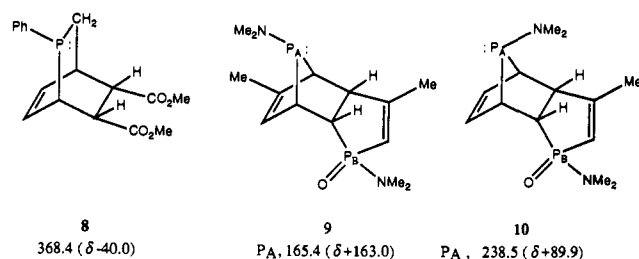
remains about the same but the shift is in the normal phosphine region. The double bond is therefore clearly implicated in the deshielding effect. The size of the saturated component of the ring system is also critical;⁹ when this size is expanded from two to three carbons, as in **6**, an upfield shift occurs, and with four carbons (**7**) the shift becomes normal for a tertiary phosphine and there is no difference in the values for the *syn* and *anti* isomers. The effect vanishes when the phosphorus-containing bridge is expanded by one carbon (**8**).¹³ The deshielding effect is also present



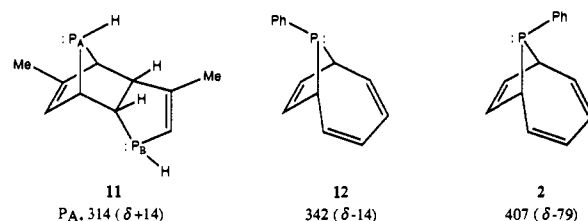
in 7-phosphanorbornenes when the alkyl or aryl substituent on phosphorus is replaced by an amino substituent¹⁴ (compounds **9** and **10**), and

(13) Quin, L. D.; Hughes, A. N.; Kisalul, J. C.; Pete, B. *J. Org. Chem.* **1988**, *53*, 1722.

replacement of H on P in an *anti* position (as in **11**) gave a secondary

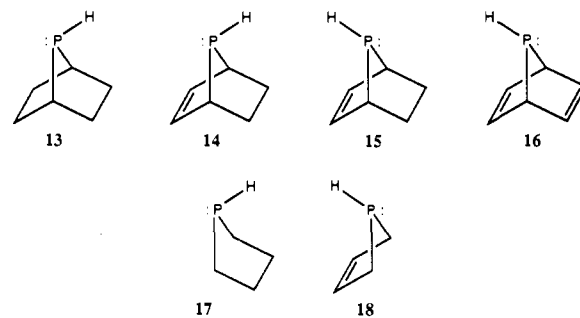


phosphine with the characteristic pronounced deshielding. When the lone electron pair on phosphorus in the 7-phosphanorbornenes is utilized in a covalent bond, as in phosphine oxides, some downfield shifting is still quite apparent¹⁰ (about 20–30 ppm), but the difference between *syn* and *anti* isomers is negligible. Another peculiar effect among unsaturated bridged phosphines had been noted years earlier by Katz⁴ and also has remained unexplained; when two additional double bonds are present in a four-membered ring component, the ³¹P shieldings are found at remarkably *high* field, but again with the *syn* isomer (**12**) more deshielded than the *anti* (**2**), by an amount (65 ppm) like that in the 7-phosphanorbornenes.



Computational Details

Shielding calculations were carried out employing Ditchfield's gauge-including atomic orbital (GIAO) coupled Hartree-Fock method¹⁵ on the four bicyclic phosphorus compounds 7-phosphabicyclo[2.2.1]heptane (**13**, *ndb*), 7-phosphabicyclo[2.2.1]heptene (**14**, *anti*, and **15**, *syn*), and



7-phosphabicyclo[2.2.1]heptadiene (**16**, *2db*), as well as the monocyclic saturated five-membered ring phospholane (**17**, tetrahydrophosphole, *thp*) and the unsaturated five-membered ring 3-phospholene (**18**, 2,5-dihydrophosphole, *2,5-dhp*); the shortened abbreviations for these compounds are used for ease of reference in the data tabulations. Calculations were also carried out for the methyl derivatives of **14** and **15** and confirmed that the simpler hydrogen compounds provided the same basic effect as the bulkier methyl group. The basis sets employed were the valence triple- ζ with polarization (6-311G(d,p)) for carbon and hydrogen¹⁶ (a [4s,3p,d/3s,p] basis with six cartesian d functions) and the McLean-Chandler 12s, 9p basis¹⁷ in the contraction (63111/4211) = [6s,5p] for phosphorus with either one or two sets of (six) d polarization functions. A single set of d functions was employed for phosphorus for the structural optimizations using the standard exponents in the Gaussian 92 code;¹⁸ for the chemical shielding calculations two sets of d functions were used for phosphorus where the standard exponent (0.55) was multiplied and divided by a factor of 2 as suggested by Frisch et al.¹⁹ so

(14) Szweczyk, J.; Quin, L. D. *J. Org. Chem.* **1987**, *52*, 1190.

(15) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.

(16) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(17) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

that the d-exponent ratios were always equal to four. The structures employed for the shielding calculations were optimized at the level of basis indicated above, and all molecules were required to exhibit C_2 symmetry. Methylene hydrogens (CH_2) were constrained to have equal CH bond distances and CCH bond angles in all the structures with the exception of the monocyclic five-membered ring compounds, where the hydrogens on the carbon α to the phosphorus atom were permitted to have different PCH bond angles. All dihedral angles were allowed to vary.

Except as noted, chemical shieldings calculated here are reported as absolute values. While experimentalists tend to report relative displacements of the NMR lines (relative to some standard, which in the case of phosphorus is typically 85% phosphoric acid), normally called "chemical shifts", δ , theoretically one determines an "absolute" displacement, usually referred to as "chemical shielding", σ . The latter is really a shift with respect to the bare nucleus and is such that more positive values indicate diamagnetic or upfield shifts (more negative δ -values) and more negative values indicate paramagnetic or downfield shifts (more positive δ -values). We usually indicate both types of results by indicating relative chemical "shifts" in parentheses and preceding them with the symbol δ and a sign (+/-) indicating the shift relative to phosphoric acid, whose absolute shift has been determined to be 328.4 ppm;² experimental shifts have been converted to absolute shieldings using this value for phosphoric acid. The advantage of absolute shifts is that systematic errors are not hidden by a relative comparison, and, of course, relative shifts, if desired, are easily obtained from the absolute values.²⁰

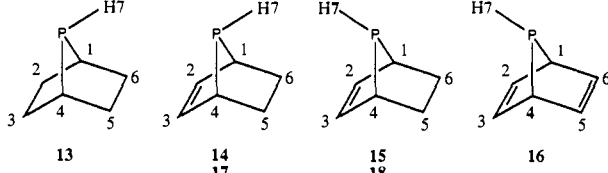
The molecular orbitals were analyzed using modules designed for the Convex Applications Visualization System (AVS) and a partitioning program designed to divide the shielding into atomic and molecular orbital contributions. All the calculations were carried out on a Cray Y-MP located in the North Carolina Supercomputing Center.

Results and Discussion

A. Results. Optimized molecular configurations are employed in the current study, since most of the structures are unknown experimentally. Since the crystal structure of the phenyl derivative of **4** has been determined,²¹ a measure of the reliability of our model structures can be obtained by comparing parameters in this structure to those calculated for the *anti* structure (**14**). The heavy-atom bond lengths and angles in the common bicyclic framework of the two molecules agree on average to better than 0.01 Å and 1.0°, agreement which is quite good for a structure of this general complexity.

Absolute shielding values for phosphorus and all other nuclei in the six molecules studied are given in Table I along with pertinent data concerning several important structural angles. The absolute shielding values for the *anti* and *syn* species (**14** and **15**) are probably best compared to the experimental results for the methyl derivatives of molecules **3** and **4** and the phosphine **11**, where it is seen that the calculated shieldings for both the hydrogen derivatives (as well as the two methyl derivatives) are some 40–50 ppm too high on an absolute basis. The GIAO method in the basis employed here tends to yield phosphorus shieldings that are on average some 14–15 ppm high and show a root mean square error of some 25–30 ppm when compared to absolute gas-phase measurements.^{6,7} Given this noise level of current Hartree-Fock calculations for phosphorus, the above agreement on an absolute basis can be considered satisfactory, especially since the molecules compared are not identical. Of greater significance, however, is the change in shielding in moving from the *anti* to *syn* forms. Our calculations give a downfield shift of 95.9 ppm (84.9 for the methyl derivative) to be compared to the

Table I. Absolute Shieldings (ppm) and Angles (deg) for the Optimized Phosphorus Bicyclic and Monocyclic Structures^a



	ndb (13)	<i>anti</i> (14)	<i>syn</i> (15)	2db (16)	thp (17)	2,5-dhp (18)
A. Absolute Shieldings						
P	409.6	365.4 ^a	269.5 ^b	142.3	420.0	434.8
C1 ^c	161.7	159.3	158.1	152.0	172.9	169.7
C2	169.2	54.3	48.0	41.2		58.1
C6	165.4	167.4	171.2	47.4	169.8	
H7 ^d	29.68	28.62	28.62	26.64	29.53	29.15
H1	30.48	30.01	30.03	29.52	31.08 ^e	30.25 ^e
H2(exo)	30.97	26.02	25.73	25.04		26.30
H2(endo)	31.30					
H6(exo)	30.92	30.61	30.54	25.17	30.91	
H6(endo)	31.10	31.05	31.21		30.65	
B. Angle Data						
H7PC1	99.9	100.3	99.9	100.7	97.5	96.7
C1PC4	80.0	79.3	79.1	77.7	89.6	92.3
flap-1	126.0	124.5 ^f	129.1 ^g	125.8	145.0	166.6
flap-2	119.0	120.0 ^f	116.4 ^g	115.4		

^a Shielding value for the methyl derivative is 351.3 ppm. ^b Shielding value for the methyl derivative is 266.4 ppm. ^c Carbon shieldings may be converted to shifts relative to liquid TMS using its absolute shielding of 184.1 (Jameson, A. K.; Jameson, C. J. *Chem. Phys. Lett.* **1987**, *134*, 461). ^d Proton shieldings may be converted to shifts relative to aqueous CH_4 by using its absolute shielding of 30.61 (Raynes, W. T. In *Nuclear Magnetic Resonance*; Harris, R. K., Ed.; The Chemical Society: London, 1978; Vol. 7, p 1). ^e Average of the equatorial and axial hydrogens. ^f Flap-1 and -2 values for the corresponding methyl derivative are 126.8° and 118.1°, respectively. ^g Flap-1 and -2 values for the corresponding methyl derivative are 130.6° and 115.3°, respectively. ^h The atom numbering is as shown below in the drawing of the basic framework; numbering for the five-membered rings follows the appropriate sections of the two innermost drawings.

experimental results of 74.3 ppm for the methyl derivatives of **3** and **4**, of 71.3 ppm for the phenyl derivatives of **3** and **4**, and of 73.1 for the dimethylamine derivatives of **9** and **10**. We note in addition that species **5** (with no unsaturation in the bicyclic ring) is shifted upfield by some 118.8 ppm with respect to the (*syn*) methyl derivative of **3** while the calculated difference between our ndb (**13**) and *syn* (**15**) cases is 140.1 ppm. It is apparent that the theoretical calculations are reproducing the effects seen experimentally and that an analysis of these data should provide a basis for an understanding of the underlying physical causes.

Upon optimization the structures obtained for the various species show very reasonable bond lengths and angles (not given) that, with the exception of the flap angles to be discussed, show very little change within the bicyclic (or the monocyclic) structures. In particular, as shown in part B of Table I, the geometry about the phosphorus atom in the bicyclic structures as revealed by the H7PC1 and C1PC4 angles exhibits very little variation and therefore is *not* an indicator of the corresponding shielding changes seen throughout this series of molecules.

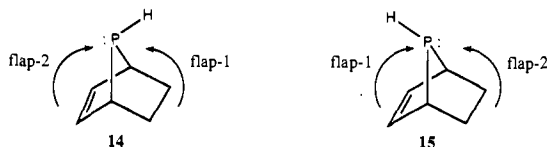
The flap angles do, however, serve as an indicator of the underlying cause of the shielding changes, as we discuss below, and they do change in a significant way across the species studied. The flap angles are those of the bridging CPC part of the ring systems (in both the bicyclic and monocyclic species). Flap-1 is defined as that flap angle on the side of the CPC bridge that contains the phosphorus hydrogen (or methyl group), and flap-2 is the flap angle for the opposite side. Thus, as shown below, flap-1 relates to the double-bond side in the *syn* case (**15**) but to the saturated side in the *anti* molecule (**14**). Note that the sum

(18) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, revision C.; Gaussian, Inc.: Pittsburgh, PA, 1992.

(19) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(20) Employing the basis sets used here, a shielding of 332.9 ppm is calculated for PO_4^{3-} ; see ref 6.

(21) McPhail, A. T. Private communication.



of the two flap angles is virtually constant for the four bicyclic structures and that the flap-1 angle is always significantly larger than flap-2 by some 9° on average.²² This clearly suggests that the interaction of the phosphorus H (or CH_3) with either the double bond or the saturated CC linkage in the other ring is stronger than that of the lone pair. The angle difference by itself does not indicate whether the interaction is more repulsive or less attractive, but one would expect the coupling to be repulsive, arising as it does from two filled-shell subsystems of a molecule. In their (relaxed) optimized forms, the *syn* phosphanorbornene species is calculated to be higher in energy than the *anti* form by only 2.39 kcal/mol.

We note that, in the case of the monocyclic compounds with no (2,5-dhp, 17) and one (thp, 18) double bond, the (single) flap angle opens up considerably to relieve the strain forced upon the system in the case of the bicyclic structures. Note also that the chemical shielding in the five-membered rings is moved significantly upfield of the predicted resonances of the bicyclic structures containing one (*anti* 14, and *syn*, 15) or two (2db, 16) double bonds and is comparable to that of the unsaturated phosphorbornane (ndb, 13).

As we discuss in greater detail below, the small flap angles are at the base of the underlying physical cause of the shielding differences seen in these species and are controlled by the interaction of the phosphorus hydrogen with the saturated or unsaturated portion of the molecule beyond the bridging (α) carbons.

B. Key Aspects of Paramagnetic Shielding. As is true of many quantities in quantum mechanics, the underlying physics is deceptively simple while the actual quantum mechanical calculation and understanding is often quite complex. This is certainly true of chemical shielding. It is, therefore, very satisfying when one can readily relate shielding effects to fundamental causes such as is the case in the present study. Because of this, we feel it appropriate to discuss key aspects of NMR shielding in general as well as in particular as they apply to the present molecules of interest.

Chemical shielding is caused by magnetic fields induced in the molecule by the application of an external magnetic field. Charge clouds are set in rotation as one turns on an external magnetic field, and the external field also tends to provide net currents in the molecule, as the energies of electrons with equal and opposite angular momenta now differ. Contributions to the chemical shielding are usually divided into so-called diamagnetic and paramagnetic parts, an arbitrary but often useful division. In the case of Ditchfield's GIAO approach, this division may be made by defining as "diamagnetic" those contributions which are linear in the zeroth-order (unperturbed) density matrix and by terming those contributions "paramagnetic" which are linear in the first-order perturbed density matrix. It has been known for some time that the paramagnetic terms generally dominate changes in shielding for a particular nucleus as its molecular environment is modified. This is certainly true for the species calculated here, where the overall shielding changes by nearly 300 ppm while the total range of the diamagnetic shieldings is a trivial 1.0 ppm.

The paramagnetic contribution comes about from the coupling of the external field term ($H \cdot L$) between orbitals unoccupied in

(22) The crystal structure of the phenyl derivative of 4 (see ref 21) exhibits average (of two) flap-1 and -2 angles of $125.8 \pm 118.0 \pm 0.6^\circ$, respectively, to be compared to the values of 124.5° and 120.0° calculated for species 14 (and 126.8° and 118.1° for its methyl derivative). The average experimental CPC angle is found to be $79.3 \pm 0.3^\circ$, in exact agreement with that calculated for 14 of 79.3° .

the Hartree-Fock ground state and those normally filled. The $H \cdot L$ operator acts like a rotation operator (dependent on the angular momentum quantum number) and will, for example, convert a p-function pointing in the x -direction into one pointing in the y -direction when the external field is along the z -axis of the system. Strong paramagnetic effects are then to be expected when orbitals have large coefficients in those molecular orbitals which are coupled by this operator. The more localized the molecular orbitals containing the rotationally related atomic orbitals tend to be, the larger will be the coupling. For example, one of the causes of the large paramagnetic shielding for double-bonded carbon is the localized nature of the $p \pi$ orbitals.

Because the theoretical approach involves perturbation theory, the coupling between molecular orbitals also depends upon the difference in orbital energies involved. Since basically one is coupling orbitals that are normally unoccupied with those which are normally occupied, one might expect that the smaller the HOMO-LUMO gap the more likely strong paramagnetic shielding can be realized. Citing again the example of double-bonded carbon, the HOMO-LUMO gap in such systems is small because of the nature of π orbitals tending to lie at higher orbital energies as well as the π^* orbitals tending to lie at the lower energy end of the unoccupied set. Indeed, this qualitative dependence upon the energy gap is the basis for the old average energy approximation used in shielding calculations 30 years ago.²³

Application of these basic ideas to the present molecules is seen when one breaks down the contribution to the shielding in terms of the molecular orbitals which are coupled and their relative positions along the orbital energy axis. In the neutral phosphines investigated here, one has a lone pair which will tend to dominate MOs lying close to the energy gap; likewise, the π orbital will contribute strongly to states close to the gap as will the π^* orbital to the low-lying virtual states. As we shall see, it is the movement of these levels determined mainly by the interactions involving the phosphorus hydrogen that determines the order and range of shielding. Figure 1 shows two views of the computer-generated surface for the HOMO in the *syn* compound 15 and demonstrates the dominance of the lone pair and π orbitals in this molecular orbital.

Another aspect which is important in the present situation is a strong contribution (along with the π^* orbital) to the low-lying unoccupied levels in all the molecules studied of a p orbital on phosphorus lying perpendicular to the C_s plane of symmetry and having the same symmetry as the π^* state. Figure 2 shows two views of the computer-generated surface for the LUMO in the *syn* compound 15 and shows the dominance of the phosphorus p and carbon π^* orbitals in this molecular orbital.

That is to say, the molecular orbitals which tend to dominate the shielding here are those dominated by the lone pair and π bonding orbitals of the high-lying occupied levels and by the phosphorus (perpendicular) p orbital and π^* levels of the low-lying virtual states. This localization of the rotationally related phosphorus atomic orbitals and the nearness in orbital energy of the shielding dominating molecular orbitals present a potent combination for deshielding (shifts to lower fields).

The situation is shown graphically in Figure 3 for the four bicyclic compounds 13-16, where the high-lying occupied and low-lying unoccupied orbitals are seen to be dominated by the phosphorus lone pair (Lp) and p orbital perpendicular to the C_s plane of symmetry (p) and the carbon double bond π (π) and π^* (π^*) contributions. The levels for the occupied states shown are contiguous in orbital number, while above the LUMO orbital shown there are one or two vacant states (of different symmetry, not shown) separating the other π^* -dominated MOs. As expected, these MOs containing components as strong as the lone pair, p , and π and π^* orbitals lie near the HOMO-LUMO gap, and their

(23) Karplus, M.; Das, P. T. *J. Chem. Phys.* 1961, 34, 1683.

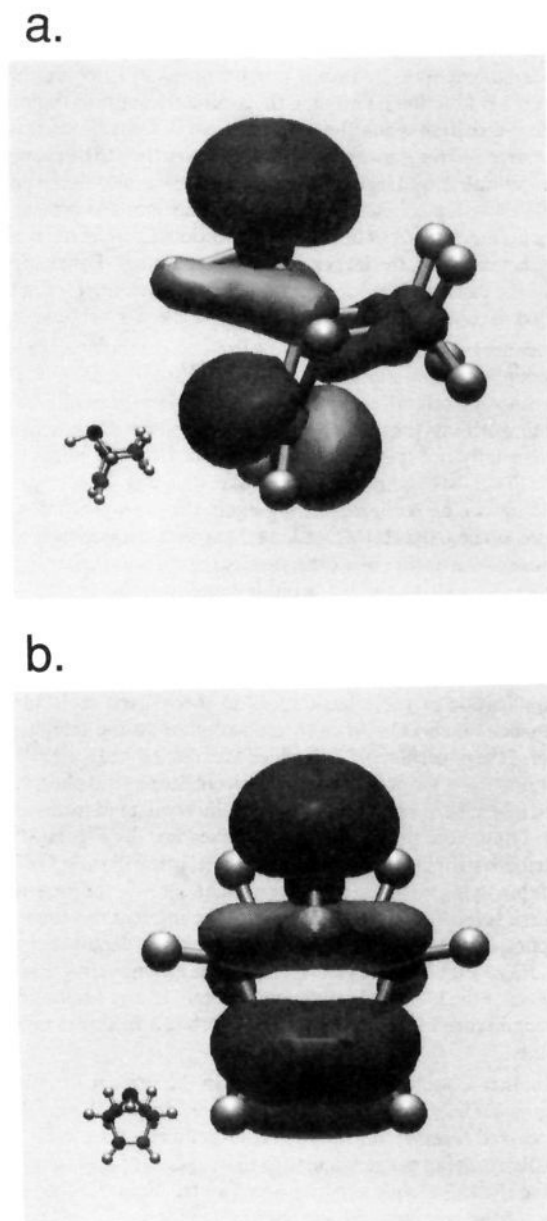


Figure 1. Computer-generated surfaces for the *syn* (**15**) HOMO molecular orbital (a) looking nearly perpendicular to the C_s symmetry plane and (b) viewed along an axis (in the symmetry plane) perpendicular to the carbon-carbon double bond. A large-amplitude surface is shown to demonstrate the dominance in the HOMO of the phosphorus lone pair and bonding carbon-carbon π orbitals. The different shadings correspond to the differing signs of the MO in different regions of space.

relative position determines the gap energy, $E_g = E[\text{LUMO}] - E[\text{HOMO}]$. HOMO and LUMO orbital energies are given in Table II.

For the saturated case (ndb, **13**), a single occupied lone-pair-dominated orbital occurs as HOMO, and a mainly p unoccupied orbital, as the LUMO. The addition of a double bond to the system in the *anti* configuration (**14**) causes both of these orbitals to split and to now contain π or π^* components; the HOMO is raised and the LUMO lowered by this coupling and, since these MOs tend to dominate the shielding, a paramagnetic shift in the resonance occurs from 409.6 ppm ($\delta -81.2$) to 365.4 ppm ($\delta -37.0$); see Table I. The splitting of the levels is relatively small, reflecting the fact that the lone-pair double-bond interaction is apparently relatively weak. When the phosphorus hydrogen is placed in a *syn* arrangement (**15**), the larger interaction of the

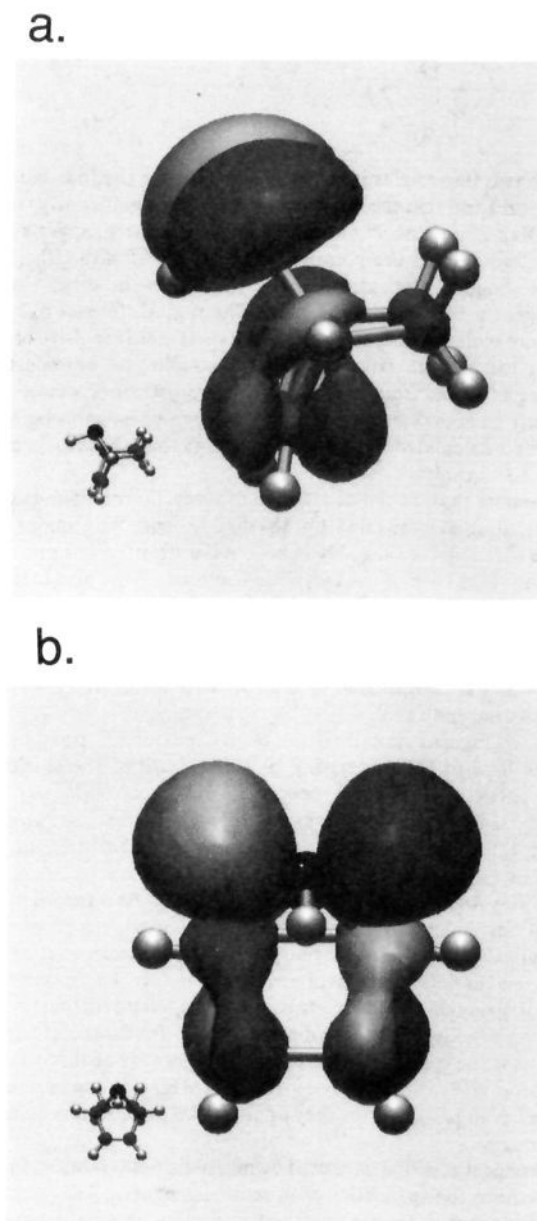


Figure 2. Computer-generated surfaces for the *syn* (**15**) LUMO molecular orbital (a) looking nearly perpendicular to the C_s symmetry plane and (b) viewed along an axis (in the symmetry plane) perpendicular to the carbon-carbon double bond. A large-amplitude surface is shown to demonstrate the dominance in the LUMO of the phosphorus p and antibonding carbon-carbon π^* orbitals. The different shadings correspond to the differing signs of the MO in different regions of space.

phosphorus hydrogen with the double bond causes these occupied levels to split considerably more, and the HOMO level is moved up; there is essentially no lowering of the LUMO level, since the PH interaction there is absent due to the different symmetry (A' compared to A''). However, the gap energy, E_g , is lowered significantly, leading to a sizable paramagnetic shift of 269.5 ppm ($\delta +58.9$) in the *syn* case compared to 365.4 ppm ($\delta -37.0$) in the *anti* case. The effect of adding a second double bond (the 2db case, **16**) is to add additional π - and π^* -dominated states to those previously present. While this doesn't significantly modify the energies of the occupied states (still a strong coupling between the phosphorus hydrogen and one of the π bonds), it does effect a lowering of the LUMO energy, thereby reducing E_g even further. The corresponding result is to further shift the phosphorus resonance downfield from 269.5 ppm ($\delta +58.9$) in the *syn* molecule to 142.3 ppm ($\delta +186.1$) in the diene (2db, **16**) case.

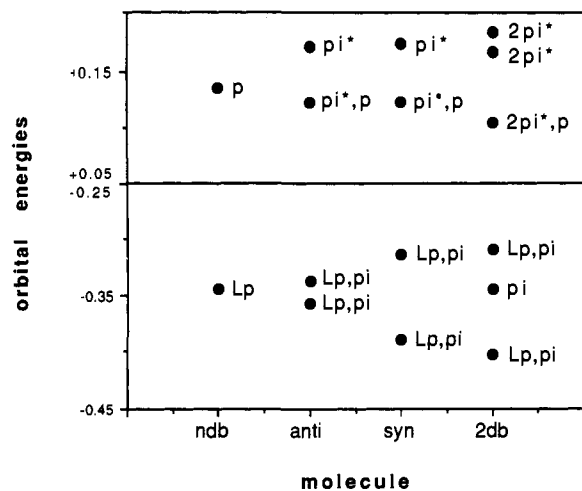


Figure 3. Representation (to scale) of the orbital energies of the high-lying occupied and low-lying unoccupied molecular orbitals for the four bicyclic molecules studied. The dominant contributions to the MOs are indicated by Lp (lone pair), pi (π), pi* (π^*), and p (a phosphorus p orbital). The occupied orbitals shown are contiguous in orbital number, while there are several states (of different symmetry) separating the LUMO and the other p- and π^* -dominated unoccupied states shown.

Table II. HOMO and LUMO Energies (au) for the Phosphorus Bicyclic and Monocyclic Structures

molecule	$\epsilon(\text{homo})$	$\epsilon(\text{lumo})$
ndb (13)	-0.343 57	0.135 70
anti (14)	-0.336 79	0.123 08
syn (15)	-0.313 22	0.121 85
2db (16)	-0.309 79	0.104 66
thp (17)	-0.343 37	0.134 47
2,5-dhp (18)	-0.347 30	0.134 82

We see then that it is the stronger interaction of the PH group with the double bond(s) relative to the lone-pair double-bond interaction that determines the energies of those MOs dominating the chemical shielding and, accordingly, provides a basis for understanding the wide range of deshieldings seen as one progresses through the ndb, *anti*, *syn*, and 2db cases. As was indicated before, this stronger PH interaction not only with the double bond(s) but also with the saturated portion of the molecules is reflected in the larger flap angle (flap-1) in all cases.

Just as the interactions between the carbon-carbon double bond and the phosphorus hydrogen and lone pair cause the movement of the orbital energy levels that leads to the deshielding effects for phosphorus, the same coupling and energy level movement should be reflected by parallel shifts for the doubly bonded carbon. The data in Table I for this carbon (C2) show that, indeed, its shielding is virtually linear in and parallel to the shielding for phosphorus. The *anti*-to-*syn* shift of 6.3 ppm downfield calculated here does not agree with the experimental trends,⁹ which indicate about a 2.4 ppm shift upfield; however, the systems studied experimentally have a more extended and complex structure and in some cases exhibit shielding differences between the two doubly bonded carbons themselves of as much as 15–20 ppm. There are evidently other, stronger effects present in the experimental systems that override the shielding effect predicted by theory for the simpler systems.

C. Five-Membered Ring Compounds. If the strong phosphorus hydrogen interaction with the other ring portions of the bicyclic compounds is permitted by a relatively small flap angle (120–130°), opening up this flap angle should reduce or remove the effect. With this in mind, calculations were carried out on the two five-membered (monocyclic) species, the saturated phospholane (17, tetrahydrophosphole (thp)), and the unsaturated 3-phospholene (18, 2,5-dihydrophosphole (2,5-dhp)). As the data for the optimized monocyclic structures in Table I show, removing

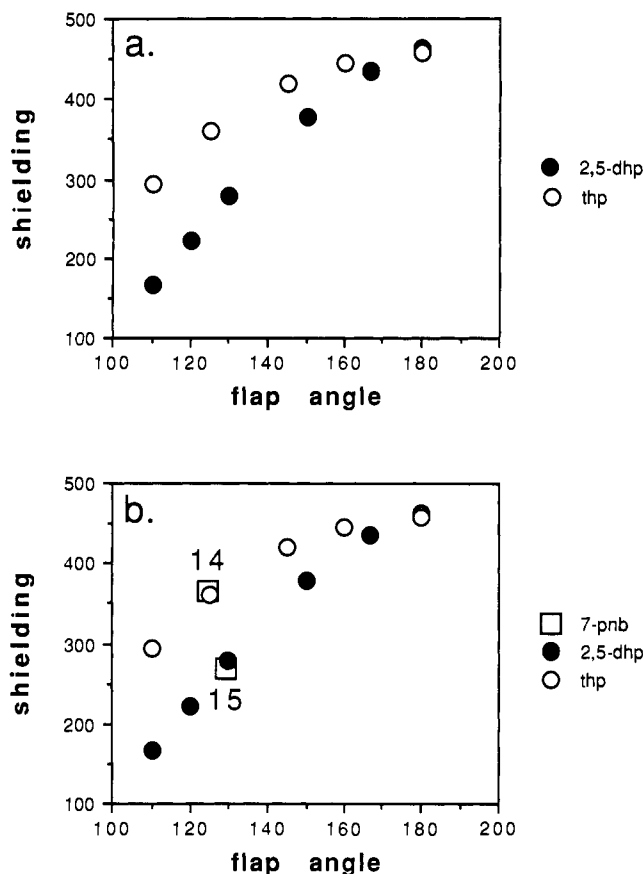


Figure 4. Shieldings as a function of flap angle for (a) the monocyclic species (thp (17) and 2,5-dhp (18) and (b) both monocyclic and 7-pnb *anti*, and *syn* compounds (14 and 15). Shieldings are given in ppm and angles in degrees.

the constraints present in the bicyclic compounds allows the flap angle to open up to 145.0° and 166.6° in these monocyclic species, the PH group is moved significantly further away from the opposing carbon portion of the molecules, essentially minimizing this interaction, and the shieldings move strongly upfield to 420.0 ppm (δ -91.6) and 434.8 ppm (δ -106.4) in these two cases. Note that in the monocyclic systems the CPC angle opens up to approximately 90° from near 80° in the bicyclic cases.

We thought it would be interesting to modify the flap angle in these two cases to see if an artificial reduction would lead to the same type of effects as seen in the bicyclic cases, where it occurs naturally. Without any further optimization, the flap angle in the two molecules was modified and the resulting shieldings are shown graphically in Figure 4a. Indeed, as one closes down the flap angle in both the saturated and unsaturated cases, the shieldings move downfield, as our earlier rationalization would predict. Figure 4b exhibits the same data but now with the *syn* and *anti* bicyclic shielding points included. One would expect the *anti* shielding to be more like the saturated (thp) case in that the PH group in both situations "sees" more strongly the saturated portion of the carbon framework; as shown, the *anti* bicyclic point falls on the curve for the saturated five-membered ring. Likewise, the *syn* bicyclic shielding should be most like that found for a comparable flap angle for the unsaturated (2,5-dhp) case, and it, too, falls nicely along the appropriate curve. Since in these studies with the monocyclic structures only the flap angle is being changed and not the CPC angle, this further confirms the lack of a significant role in the shielding variation of the CPC angle. Finally, one should note that the shift of the two shielding versus flap angle curves indicates that coupling of the PH group with the double bond is more efficient in causing deshielding than its interaction with the saturated portion of the system.

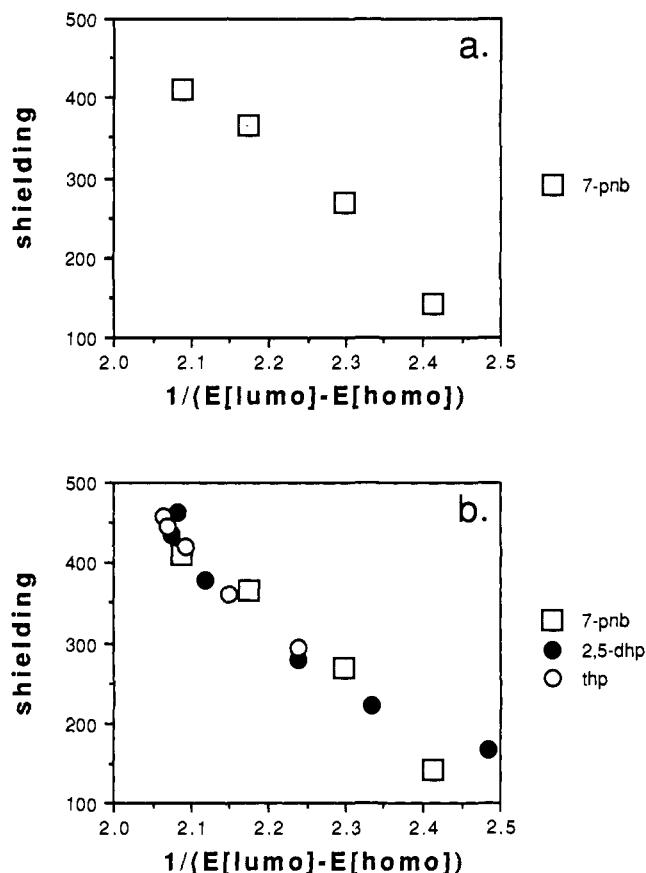


Figure 5. Shieldings as a function of the inverse energy gap, E_g^{-1} , for (a) the four bicyclic species (7-pnb, 13–16) and (b) for the bicyclic compounds and all the flap-angle-varied monocyclic species (2,5-dhp and thp). Shieldings are in ppm and energies in atomic units.

D. Dependence of the Shielding on the HOMO–LUMO Energy Gap. The parallel between changes in the energy gap and the shieldings in the bicyclic compounds suggests that in these cases one might expect to find a simple relation between these two quantities. Figure 5a shows a plot of shielding versus the inverse of the energy gap, E_g^{-1} , for the four bicyclic compounds studied, and the expected simple relation indeed emerges. If the same basic effect is present in the monocyclic molecules, one might also expect their shieldings (in both the optimized and flap-varied species) to correlate in a similar manner. In part b of Figure 5 is a second plot of shielding versus inverse energy gap that now contains not only the bicyclic compounds but also the five-membered ring species, and it is seen that, indeed, all the molecules tend to fall along the same general curve.

The average energy approximation²³ was employed out of necessity years ago due to lack of suitable calculational facilities then and because it led to expressions for shieldings that depended only on a knowledge of the ground-state wave function, a quantity that one could obtain through a variety of (often severe) approximations; the predicted shielding varied inversely as some “average” excitation energy. But, of course, if shielding in particular cases is dominated by a selected set of orbitals whose orbital energy differences differ very little, the average energy approach is qualitatively correct. Such appears to be the case in

the present study, as discussed above and as is shown by the nice dependence of the shielding on the inverse HOMO–LUMO gap energy exhibited in Figure 5.

E. Other Systems. We have seen how our present results explain nicely the phosphorus shieldings in those real compounds that have the basic bicyclo heptane framework. How do the present results and explanations apply to other bridged systems where modifications have been made to the basic bicyclic system? The *syn* and *anti* derivatives of molecules 2, 12, 6, and 7 do not show the same large downfield shielding changes but, with the exception of 7, do tend to retain about the same *syn–anti* shielding differences. Examination of models shows that enlarging the saturated two-carbon bridge from two to three or four carbons (as either a saturated or multiply unsaturated subsystem) allows the flap angle associated with the normal double-bond part of the system to open up considerably; from the flap angle dependence in the monocyclic systems studied here, we would estimate an increase in this angle of 20–30°. The PH group is now far removed from the normal double bond (just as in the flatter monocyclic compounds) and is also relatively far away from the expanded cycle due to its increased size. Accordingly, the PH–ring couplings are significantly reduced, and little deshielding is observed. Our model monocyclic flap angle variation (Figure 4) predicts a decrease of the *syn–anti* difference as the flap angle opens up, while experimentally it appears to remain about the same. This is likely due to the fact that the monocyclics studied here are different molecules than those with which the comparison is being made. It would, of course, be better to do shielding calculations on the true expanded ring systems to make a more appropriate comparison; the expanded ring sizes would, however, be much more CPU costly. Enlarging the phosphorus-containing bridge as in 8 likewise moves the phosphorus away from the other rings, reducing these interactions and the corresponding deshielding effects.

While the strong PH double-bond interaction is key to the deshielding effects seen here, the location near the HOMO–LUMO gap of molecular orbitals dominated by the lone pair is also of significant importance. As mentioned earlier, when the lone pair on phosphorus is used in covalent bond formation, as in phosphine oxides, some downfield shifting is apparent (though considerably reduced) but the difference between *syn* and *anti* isomers is negligible.¹⁰ When the lone pair is removed there is no longer that localized orbital present to contribute strongly to the *H–L* matrix element, and the deshielding effect is reduced. Although they were not analyzed extensively, we have carried out calculations on the 7-phosphanorborene and -norbornane systems where the lone pair is protonated so that one has a PH_2^+ cationic species. Removal of the lone pair in this way causes the differences between the ndb and *syn = anti* case (the two being equivalent in the protonated compound) to now be only 27.2 ppm (375.3 and 348.1 ppm) compared to a mean difference in the neutral case of 92.2 ppm. The shielding difference between the *syn = anti* cation and the 2db cation is reduced to 50.7 ppm (348.1 and 297.4 ppm), compared to 175.2 in the neutral species. As is observed experimentally, removal of the lone pair considerably reduces the range of shieldings.

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