# The Variation of Vicinal $^{31}$P–C–C–$^{1}$H Couplings with Dihedral Angle in Phosphonates[1]

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**Abstract:** Several examples of phosphonates with rigid geometries provide definite evidence for a Karplus-type variation of $^{31}$P–C–C–$^{1}$H couplings in phosphonates. The coupling is maximum for a 0 (~18 Hz) and a 180° dihedral angle (~41 Hz) and minimum for a 90° angle.

Evidence for the dihedral angle dependence of vicinal $^{31}$P–C–C–$^{1}$H coupling was first obtained from the proton nmr spectra of steroylphosphonates some time ago.[2] Since then, other examples have been abundant in the literature and proved very useful in determining the configurations of organophosphorus compounds.[3–5] Similar dihedral angle dependence has also been shown for vicinal P–O–C–H couplings although in this case the *quantitative* dependence of this coupling on the dihedral angle is not well established.[6,7]

No X-ray structural determinations have been made on the steroylphosphonates and the angles were only estimated from molecular models.[8] In view of the known high flexibility of ring A in steroids (where the $(CH_3O)_2P(O)$ group was attached), it seemed highly desirable to prepare model compounds with rigid geometry, in order to get more reliable $^{3}J_{PH}$ values for a given angle $\Phi$ (Figure 1). This paper describes the results obtained on new compounds,[10] discusses previous data from this laboratory as well as results from the literature, and shows that vicinal P–C–C–H coupling effectively follows a Karplus-type variation[12] and that these couplings behave in much the same way as the H–C–C–H couplings.

The synthesis of the new compounds described here is reported in the Experimental Section.

## Results and Discussion

Some of the $^{31}$P–C–C–$^{1}$H vicinal couplings have been measured directly from the spectra, assuming first-order features; $^{1}$H-{$^{31}$P} decoupling experiments confirmed the assignments. In the case of compound **1**, the spectrum was too complicated for a simple analysis and only the P,$H_A$ coupling could be taken directly from the spectra. The high field part of the spectrum of compound **2** was analyzed as the superposition of two ABM spectra. The spectra of the dimethyl hexachlorocyclopentadiene vinylphosphonate adduct **7** and of its pentachloro analog **8** were analyzed with the LAOCN3 program.[13] The vicinal $^{31}$P–C–C–$^{1}$H couplings have been assumed to be positive and all the experiments done so far on tetracoordinate phosphorus compounds have confirmed this finding.[14]

The results assembled in Table I conclusively demonstrate that the $^{31}$P–C–C–$^{1}$H couplings in phosphonates are primarily a function of the dihedral angle $\Phi$. For a given dihedral angle (estimated from Dreiding molecular models), there are some variations depending on substituents and bond angles.

Table I. $^{3}J_{PH}$ (Hz) as a Function of Dihedral Angle, $\Phi$

| | Angle,[a] deg | | | | |
|---|---|---|---|---|---|
| Compd | 0 | 30 | 60 | 90 | 120 |
| **1** | | | 5[b] | | |
| **2** | 16.9 | | 6.8 | | 5.5 |
| **3** | | 8.5 | | | |
| **4** | 16.5 | 7.5 | | | 6.0 |
| **5** | | | | <0.5 | |
| **6** | | | | <0.5 | |
| **7** | 17.9 | | | | 8.1 |
| **8** | 17.1 | | | | 8.6 |
| **9** | | 9 | | | |
| **10** | | 9 | | | |
| **11** | | | | <0.5 | |
| **12** | | | | <0.5 | |
| **13** | | | | <0.5 | |
| **14** | 17.4–20.0[c] | | | | |
| **15** | | | | | 6.0–8[c] |
| **16** | 14.8–15.5[c] | | | | |
| **17** | | | | | 3.5–4.2[c] |

[a] Estimated from Dreiding models. [b] Measured directly from the spectrum ±1 Hz. [c] Depending on R, see ref 4b and 4c.

**Influence of Substituents.** Although there are not enough examples of different $\alpha$ substitution, it seems

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(1) (a) Nmr of Phosphonates, part VI. For part V see ref 11. (b) Supported by the National Research Council of Canada (Grant A-5496).

(2) C. Benezra and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1825 (1966).

(3) (a) L. Evelyn, L. D. Hall, P. R. Steiner, and D. H. Stokes, *Chem. Commun.*, 576 (1969); (b) *Org. Magn. Resonance*, **5**, 141 (1973).

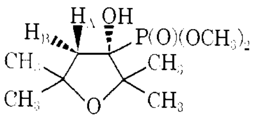
(4) (a) H. J. Callot and C. Benezra, *Can. J. Chem.*, **48**, 3382 (1970); (b) *ibid.*, **50**, 1078 (1972); (c) H. Cohen and C. Benezra, *Org. Magn. Resonance*, **5**, 205 (1973).

(5) T. Bottin and J. Seyden-Penne, *Tetrahedron Lett.*, 1945 (1972).

(6) D. W. White and J. G. Verkade, *J. Magn. Resonance*, **3**, 111 (1970).

(7) L. D. Hall and R. B. Malcolm, *Can. J. Chem.*, **50**, 2092 (1972), and references therein.

(8) X-Ray measurements have been made on a simple phosphonate, 3-dimethylphosphono-3-hydroxy-2,2,5,5-tetramethyltetrahydrofuran,[9] confirming the earlier assumptions[2] of ~30 and 90° for the angles P,$H_A$ and P,$H_B$, respectively. The spectrum of this compound has been measured again at 100 MHz and was analyzed as the superimposition of two AB subspectra, with the following results: $J_{AB}$ = 13.5 Hz, $J_{P,A}$ = 8.1 Hz, $J_{P,B}$ = 0.3 Hz, and $\delta_A$ 2.48 ppm, $\delta_B$ 2.18 ppm. The $J_{P,H}$ coupling constants measured directly on the spectra were 8.0 and <0.5, respectively. A 7.0 $J_{P,A}$ value was described[2] as measured directly from the 60-MHz spectrum.



(9) G. Samuel and R. Weiss, *Tetrahedron* **26**, 2995, (1970).

(10) A preliminary account of this work has appeared.[11]

(11) C. Benezra, *Tetrahedron Lett.*, 4471 (1969).

(12) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959).

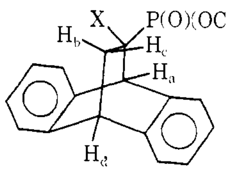
(13) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 41, 3863 (1964). We thank Dr. M. St. Jacques and M. Bernard for carrying out these two analyses for us.

(14) E. Duval and E. A. C. Lucken, *Mol. Phys.*, **10**, 499 (1966).

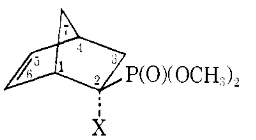
clear that $\alpha$-hydroxyphosphonates (*e.g.*, **2** and **4**) show vicinal P,H couplings which are smaller than those in phosphonates without electronegative $\alpha$ substituents (*e.g.*, 7 and **8**).

This can be ascribed to the electronegativity of the OH group.[15] This variation is small (0–1 Hz), especially when one considers how dependent on electronegativity the $^3J_{FH}$ couplings[16] appear to be for example. A notable exception seems to be the case of the $\Delta^1$-pyrazolines (**14**) where $^3J_{PH}$ can be as high as 20.0 Hz, in spite of the presence of the electronegative azo, $-N{=}N-$ substituent. It is probably not quite adequate to compare these compounds with the others, in view of the fact that for **14** there may be a second coupling path for $P,H_{10}$ coupling, through *six* bonds, *i.e.*, $P—C_3—N{=}N—C_9—C_{10}—H$. Since the homoallylic coupling between P and $H_9$ is quite important (4 to 7 Hz[4c]), it is reasonable to think that the six-bond contribution to $P,H_{10}$ coupling is not negligible.

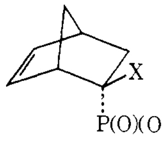
**The Effect of H-C-C and P-C-C Bond Angles.** For a 0° dihedral angle, the $^{31}P-C-C-^1H$ coupling varies between 14.5 and 20.0 Hz. Clearly, if one compares this coupling in six- (compounds **1** and **2**) or five-membered rings (most of the compounds) with the corresponding one in the three-membered ring (**16**), there is a considerable increase in internal bond angles which results in a substantial drop of the coupling from ~18 to 14.5–15 Hz. This result is quite similar to that for $^3J_{HH}$.[17a] The coupling for a ~120° angle showed a similar trend as can be seen by comparing compound **8** (~8.6 Hz) with **17** (~4.25 Hz for R = $C_6H_5$). The effect is more dramatic with $sp^2$ hybridized carbons, *i.e.*, $P—C{=}C—H$ coupling. We showed[13] that $^3J_{PH}$ drops from 22–23 Hz in acyclic $\alpha,\beta$-unsaturated and cyclohexenylphosphonates to 11 Hz in cyclopentenyl phosphonate. This trend was confirmed recently[19] when dimethylcyclobutenyl- ($^3J_{PH}$ = 5 Hz) and -cyclopropenylphosphonates (4 Hz) were prepared for the first time. Again the $^{31}P-C-C-^1H$ couplings in this respect behave very similarly to $^1H-C-C-^1H$ couplings.[17b]



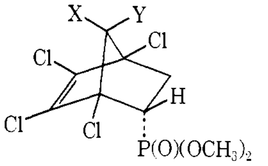
1, X = H
2, X = OH



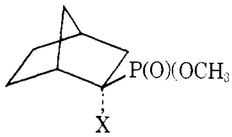
3, X = H
4, X = OH



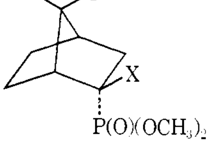
5, X = H
6, X = OH



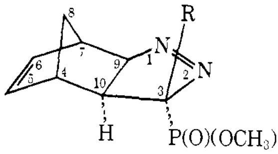
7, X = Y = Cl
8, X = H; Y = Cl



9, X = H
10, X = OH



11, X = Y = H
12, X = OH; Y = H
13, X = OH; Y = Br



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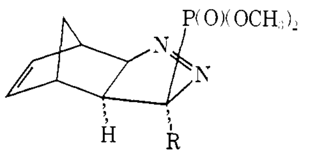

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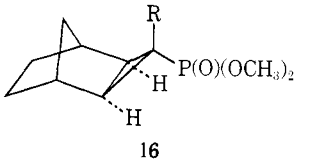
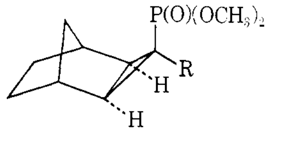


16



17

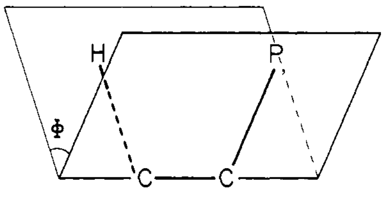


Figure 1. Dihedral angle Φ.

**Dihedral Angle.** The values for a 0° dihedral angle vary between 14.5 and 20.0 Hz. All the systems presented here show some internal strain; the least strained one probably being the bicyclo[2.2.2]octadiene system of compounds **1** and **2**. For reasons which have been disclosed above, the high values (19.0–20.0 Hz) for pyrazolines **14** may not be the result of *one* $3\sigma$ bond path, so that the best value for a zero-degree angle in an acyclic strain-free system is probably of the order of 18 Hz. This value is significantly smaller than that for $sp^2$ hybridized carbons, where, for phosphonates, $^3J_{PH}$(cis) is about 22 to 25 Hz.[18,20]

The couplings found for a ~30° dihedral angle (7.0 to 9.0 Hz) are probably smaller than can be expected from $^3J_{PH}(30°)$ coupling in a strain-free system. They all correspond to $C_2-P_{exo}$, $C_1-H$ couplings with particularly high bond angles. In norbornane, the $C_2-C_1-H$ angle is significantly higher than the normal tetrahedral angle, thus contributing to a decrease in the P,H coupling. In norbornane and norbornene derivatives, the corresponding H,H coupling ($H_1-H_{2exo}$) is smaller (3–4 Hz)[17c] than expected from a 30° dihedral angle.

There are two examples of a ~60° angle in a rigid system: in compound **1** ($^3J_{PH}$ ~ 5 Hz) and in compound **2** where the $P,H_a$ coupling is 6.8 Hz. The literature reports values of 0 to 12 Hz for gauche couplings in steroids.[2] Because of the 1,3-diaxial interaction of $CH_3-C_{10}$ and the bulky Y substituent, the *rationale* which was offered for a $^3J_{PH_2}$ ~ 0 value was that, in

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(15) A. A. Bothner-By, *Advan. Magn. Resonance*, 1, 202 (1965).

(16) K. J. Williamson, Y. F. Li Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Amer. Chem. Soc.*, **90**, 6717 (1968).

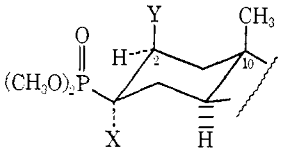
(17) (a) L. M. Jackman and S. Sternhell, "Applications of Nmr Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 286; (b) *ibid.*, p 303; (c) *ibid.*, p 288.

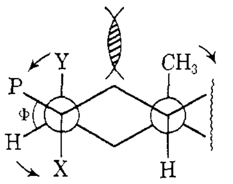
(18) C. Benezra, S. Nešić, and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1140 (1967).

(19) R. S. Marmor and D. Seyferth, *J. Org. Chem.*, 36, 128 (1971).

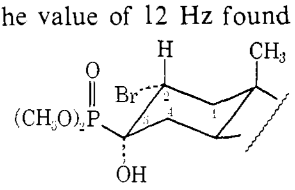
(20) G. L. Kenyon and F. H. Westheimer, *J. Amer. Chem. Soc.*, **88**, 3557 (1966); W. M. Daniewski, M. Gordon, and C. E. Griffin, *J. Org. Chem.*, 31, 2083 (1966); M. P. Williamson, S. Castellano, and C. E. Griffin, *J. Phys. Chem.*, 72, 175 (1968).

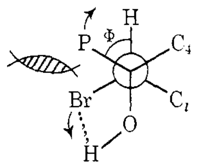
fact, Φ was near 90° in compounds **18** (X = Y = Br) and **19** (X = Br, Y = OH). This assumption was supported by the X-ray measurements made on 2β,3α-dichlorocholestane[21] for which the corresponding angle was found to be ~83°.


18 and 19



The value of 12 Hz found for compound **20** for the P,H$_2$ coupling seems particularly high. It is possible that, due to strong gauche interaction between Br and the (CH$_3$O$_2$)P(O) group, the Φ angle is caused to decrease and reach a value much lower in fact than the 60° indicated by the molecular model. This trend would be helped by the possible hydrogen bonding between Br and H–O–. In the absence of any X-ray data on this compound, this value of 12 Hz cannot be regarded as a reliable example of a 60° dihedral angle P,H coupling.

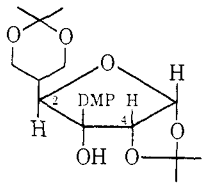

20



The 6.8 Hz found for P,H$_a$ in compound **1** can be considered as satisfactory, especially when one considers the 6.3 Hz found in an acyclic compound, chloroethylthiophosphoryl dichloride, ClCH$_2$CH$_2$P(S)Cl$_2$, for $J_{\text{gauche}}$.[22]

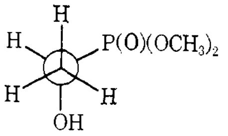
A ~90° dihedral angle arrangement as in compounds **5**, **6**, and **11–13** between phosphorus and the bridgehead hydrogen results in a negligible vicinal coupling. This finding has proved to be very useful for the study of Diels–Alder additions with dimethyl vinylphosphonate.[4a]

A ~120° angle corresponds to 5.5 to 8.6 Hz coupling (compounds **2**, **4**, **7**, **8**, etc.), while there is an example in the literature[3a] for a ~150° angle in a C–P containing carbohydrate: $^3J_{\text{PH}_2}(\sim 150°) = 28.5$ Hz in compound **21**.


21 (DMP = dimethylphosphono group)

No value for a ~180° in rigid systems was available. It is nevertheless possible to make a satisfactory estimate for such a coupling from the proton nmr spectrum of an acyclic molecule, dimethyl 1-hydroxy-1-ethylphosphonate, CH$_3$CH(OH)P(OCH$_3$)$_2$, for which there are three identical staggered conformations such as A. The observed *vicinal* P,H coupling is an average of $J_{\text{trans}}$ and $J_{\text{gauche}}$ according to eq 1.

$$J_{\text{obsd}} = {}^1/_3 J_{\text{t}} + {}^2/_3 J_{\text{g}} \tag{1}$$


A

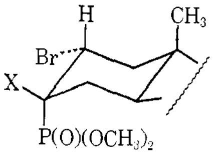
If one substitutes for $J_{\text{g}}$ the average for a 60° angle (compounds **1** and **2**), *i.e.*, 6.0 Hz, it is possible to find $J_{\text{t}}$.

$$J_{\text{t}} = 3J_{\text{obsd}} - 2J_{\text{g}}$$

Since $J_{\text{obsd}} = 17.8$ Hz, and with $J_{\text{g}} = 6.0$ Hz, it follows that

$$J_{\text{t}} = (3 \times 17.8 - 2 \times 6.0) = 41.4 \cong 41 \text{ Hz}$$

This value seems satisfactory if one considers that in steroylphosphonates **22** and **23**, $^3J_{\text{PH}}$ was found to be 35 and 33 Hz, respectively.[2]


**22**, X = Br

**23**, X = OH

Figure 2 represents the curve obtained for the equations

$$^3J_{\text{PH}} = 18 \cos^2 \Phi \qquad 0 < \Phi < 90° \tag{2}$$

$$^3J_{\text{PH}} = 41 \cos^2 \Phi \qquad 90 < \Phi < 180° \tag{3}$$

Agreement between the theoretical cos$^2$ Φ curves and experiments is reasonably good (Table II), experimental values for ~30° angle being too low and those for ~60° a little too high. Again the maximum value for a 180° angle (41 Hz) is smaller than the value of sp$^2$ hybridized systems (50 Hz).

**Table II.** Calculated and Observed $^3J_{\text{PH}}$ Couplings in Phosphonates

| Angle, deg | Calcd,[a] Hz | Obsd, Hz |
|---|---|---|
| 0 | 18 | 14.5–20.0 |
| 30 | 13.5 | 7.0–9.0 |
| 60 | 4.5 | 5–6.8 |
| 90 | 0 | <0.5 |
| 120 | 10 | 5.5–8.6 |
| 150 | 30 | 29[b] |
| 180 | 41 | 33–35[c] |

[a] From eq 2 and 3. [b] Reference 3a. [c] Reference 2.

Long-range $^{31}$P–C–C–C–$^1$H couplings in compounds **4** ($J_{\text{P,H}_6} = 3.0$ Hz), **8** ($J_{\text{P,H}_7} = 4.0$ Hz), and **13** ($J_{\text{P,H}_7} = 5.0$ Hz) are useful for configuration determinations.

In summary, the vicinal $^{31}$P–C–C–$^1$H coupling in phosphonates appears to follow a Karplus-type variation.[12] The dihedral angle seems to be the major factor contributing to this coupling although at the present time there are not enough data to ascertain with accuracy the influence of substituents and of bond angles.

## Experimental Section

The ir spectra were recorded on a Beckman 20 ir spectrometer in Nujol mulls. They are without unusual features and all show the expected P=O and P—O—C absorptions at 1230–1260 and ~1050 cm$^{-1}$, respectively. Proton nmr spectra were recorded on a HA-

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[21] H. L. Geise, A. Tieleman, and E. Havinga, *Tetrahedron*, 22, 183 (1966).

[22] A. Bothner-By and R. H. Cox, *J. Phys. Chem.*, 73, 1830 (1969).

100 Varian spectrometer using 5 to 8% solutions in deuteriochloroform while $^{31}P$ decouplings were performed at 40 MHz with an NMR Specialties heteronuclear decoupler. Chemical shifts are given in $\delta$ ppm values, using TMS as internal reference, and coupling constants are given in Hz.

The dimethyl vinylphosphonate used in this study was prepared as described previously[4a] and dimethyl phosphonate, $HP(O)(OCH_3)_2$, was an Aldrich product, used as received. Solutions of sodium methoxide in methanol were prepared by adding freshly cut sodium metal to anhydrous methanol and removing the unreacted metal after 3–4 hr. Microanalyses were performed by Dr. Daessle (Organic Microanalyses Laboratories, Montreal).

**2-Dimethylphosphono-5,6,7,8-dibenzobicyclo[2.2.2]octadiene (1).** A mixture of anthracene (2.685 g, 15.06 mmol) and dimethyl vinylphosphonate (1.299 g, 9.540 mmol), dissolved in xylene (7.5 ml) to which some crystals of hydroquinone were added, was heated in a steel bomb for 8 hr at 240° (external temperature). After cooling to room temperature, the mixture was dissolved in methylene chloride, excess anthracene was filtered off, and the crude was poured on a silica gel column chromatograph (45 g, Merck, 70–230 mesh). Elution with ether–petroleum ether (1:1) gave 0.8 g of anthracene; with pure ether, a mixture of anthracene and product (0.49 g) was obtained. The pure compound **1** was then eluted (0.43 g) followed by 0.20 g of unreacted dimethyl vinylphosphonate. In all, 0.8 g of product was obtained. Recrystallization from ether–petroleum ether gave an analytical sample: mp 97–98°; nmr ($CDCl_3$) ~7.1 (m, 8 H, H arom), 4.64 (d of broad d, 1 H, $H_a$), 4.36 (m, 1 H, $H_d$), 3.31 and 3.48 (2d, 6 H, nonequiv $POCH_3$, $J_{PH}$ = 10.0).

*Anal.* Calcd for $C_{18}H_{19}O_3P$ (314.321): C, 68.78; H, 6.09; P, 9.85. Found: C, 68.46; H, 6.30; P, 9.71.

**2-Dimethylphosphono-2-hydroxy-7,8,5,6-dibenzobicyclo[2.2.2]octadiene (2).** To a solution of dibenzobicyclo[2.2.2]octadienone[23] (86 mg, 0.39 mol) in benzene (5 ml) were added dimethyl phosphonate (55 mg, 0.50 mmol) and 10 drops of a saturated solution of NaOMe in $CH_3OH$. After 24 hr at room temperature, the mixture was poured on a silica gel column (70–230 mesh, 5.5 g). Successively eluted were unidentified colored products (14 mg, petroleum ether), followed by the starting ketone (30 mg) and a mixture (70 mg) of the hydroxyphosphonate **2** and dimethyl phosphonate (ether–methanol 8:2). This fraction was chromatographed again on silica gel and 50 mg of the hydroxyphosphonate **2** was isolated. Recrystallization in acetone provided the analytical sample: mp 152–153°; nmr ($CDCl_3$) 1.73 ($H_b$), 2.46 ($H_c$) AB part of an ABMX spectrum (M = $H_d$, X = P) with $J_{P,c}$ = 16.9, $J_{P,b}$ = 5.5, $J_{AM}$ = $J_{BM}$ = 3.0, $J_{AB}$ = 14.0; 3.90 and 3.23 (2d, nonequiv P–O–$CH_3$, $J_{PH}$ = 10.5), 4.34 (m, 1 H, $H_d$, $^4J_{PH}$ = 3.0), 4.69 (d, 1 H, $H_a$, $J_{PH}$ = 6.8).

*Anal.* Calcd for $C_{18}H_{19}O_3P$: C, 65.45; H, 5.80; P, 9.38. Found: C, 65.62; H, 5.87; P, 9.58.

**2-Dimethylphosphono-2-hydroxy-5-bicyclo[2.2.1]heptenes (4 and 6).** To a mixture of 5-norbornen-2-one (1.289 g, 12 mmol), prepared by Jones' oxidation of a commercially available (Aldrich) mixture of *endo*- and *exo*-norbornen-2-ols, and dimethyl phosphonate (1.320 g, 11.99 mmol) was added 12 drops of a saturated solution of $NaOCH_3/CH_3OH$. After 48 hr at room temperature, the mixture was chromatographed on a 40-g silica gel column. Successively eluted were (weight and eluent indicated) the starting ketone (50 mg, petroleum ether–ether 9:1) and a mixture of hydroxyphosphonates **4** and **6** (1.54 g, ether). Part of this mixture (1.18 g) was chromatographed on a 115-g silica gel column and the fractions collected with an automatic fraction collector, using ether as eluent. Pure *exo*-dimethylphosphono isomer **4** was isolated in the first fractions (0.145 g), then mixtures increasingly rich in compound **6** were eluted. The last fractions were chromatographed again using ethyl acetate as eluent and some pure (0.050 g) *endo*-dimethylphosphono adduct **6** was obtained. The compounds were analyzed as a 1:1 mixture.

*Anal.* Calcd for $C_9H_{15}O_4P$ (218.19): C, 49.54; H, 6.93; P, 14.20. Found: C, 49.35; H, 6.74; P, 14.45.

Compound **4**: mp 79–81; nmr ($CDCl_3$) 1.15 (octet, 1 H, $H_{3endo(n)}$, $J_{3n3x}$ = 12.5, $J_{3n7s}$ = 3.5, $J_{3nP}$ = 6.0), 1.66 (ABq, $H_7$, $\delta_{7a}$ 1.87, $\delta_{7s}$ 1.35, $J_{AB}$ = 9.0), 2.32 (octet, 1 H, $H_{3exo(x)}$, $J_{3x4}$ = 3.5, $J_{3xP}$ = 16.5), 3.03 (broad s, 1 H, $H_4$), 3.39 (d of broad s, 1 H, $H_1$, $J_{PH}$ = 8.5), 3.75 and 3.76 (2d, 6 H, $POCH_3$, $J_{PH}$ = 10.0), 5.13 (d, PCOH, $J_{PH}$ = 1.0), 6.06 (ABq perturbed by several protons and by $^{31}P$: $\delta_5$ 6.17, $\delta_6$ 5.95, $J_{5,4}$ = $J_{6,1}$ = 3.0, $J_{5,6}$ = 6.0, $J_{PCCCH_6}$ = 3.0).

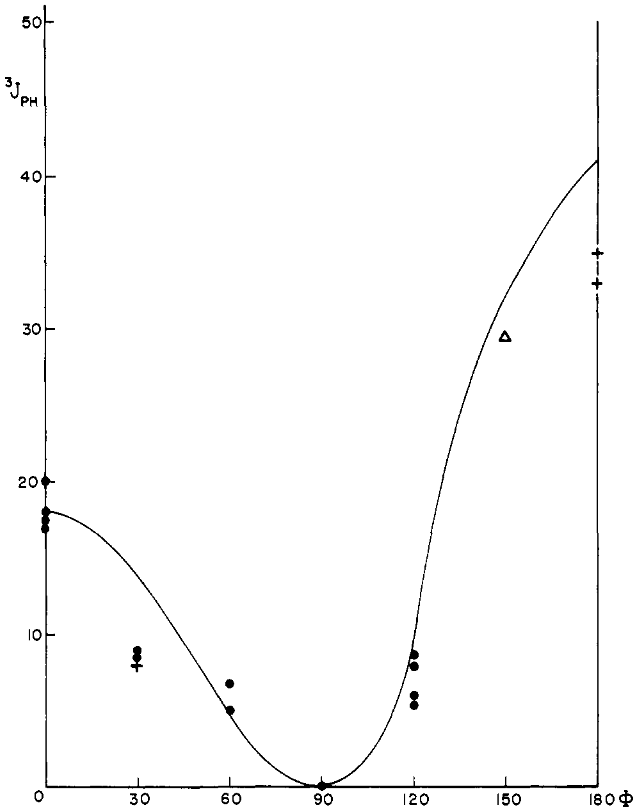


Figure 2. Curve representing the variation of vicinal P,H coupling as a function of dihedral angle: (●) data from present work; (+) data from ref 2; (Δ) data from ref 3.

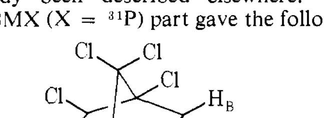
Compound **6**: oil, nmr 2.66 and 2.94 (2 broad s, bridgehead protons), 3.75 (d, 6 H, $POCH_3$, $J_{PH}$ = 10.0), 6.15 (m, 2 H, $H_5$ and $H_6$).

***endo*-2-Dimethylphosphonobicyclo[2.2.1]heptane (11).** *endo*-2-Dimethylphosphonobicyclo[2.2.1]-5-heptene[4a] (500 mg) was dissolved in 30 ml of methanol and palladium on charcoal (100 mg, 10% catalyst from Matheson Coleman and Bell) was added. The mixture was hydrogenated in a Parr apparatus at ~4 atm of pressure for 18 hr. After filtration and removal of the solvent, 500 mg of a colorless oil, shown to be pure by nmr, was obtained. An analytical sample was prepared by distillation at 85° under 0.55 Torr of pressure: nmr ($CDCl_3$) 3.71 and 3.72 (2d, 6 H, nonequiv $POCH_3$, $J_{PH}$ = 10.0), 2.50 and 2.32 (2 broad s, H-4 and H-1), 1.06–2.14 (m, 9 H).

*Anal.* Calcd for $C_9H_{17}O_3P$: C, 52.94; H, 8.33; P, 15.20. Found: C, 52.88; H, 8.27; P, 14.94.

**Compounds 10 and 12.** These have already been described.[24] Their nmr spectra at 100 M Hz (compound **10**) 4.17 (broad s, 1 H, O*H*), 3.80 and 3.78 (2d, 6 H, $POCH_3$, $J_{PH}$ = 10.0), 2.54 (d of broad s, 1 H, $H_1$, $^3J_{PH}$ = 9), 1.69–2.34 (*m*, 9 H): (compound **12**) 4.75 (broad s, 1 H, OH), 3.77 and 3.73 (2d, 6 H, $POCH_3$, $J_{PH}$ = 10.0), 2.42 and 2.28 (2m, $H_1$ and $H_4$), 1.0–2.2 (m, 8 H).

**Nmr Spectrum of *endo*-2-Dimethylphosphono-1,4,5,6,7,7-hexachloro-5-bicyclo[2.2.1]heptene (7).** The gross features of the spectrum have already been described elsewhere.[4a] The LAOCN3 analysis of the ABMX (X = $^{31}P$) part gave the following results.



$J_{AB}$ = −12.4 ± 0.09 Hz
$J_{AM}$ = 5.1 ± 0.09 Hz
$J_{AX}$ = 17.9 ± 0.13 Hz
$J_{BM}$ = 9.7 ± 0.10 Hz
$J_{BX}$ = 8.1 ± 0.14 Hz
$J_{MX}$ = −16.7 ± 0.14 Hz

$\delta_A$ 239.6 ± 0.07 Hz
$\delta_B$ 273.4 ± 0.07 Hz
$\delta_M$ 316.0 ± 0.07 Hz

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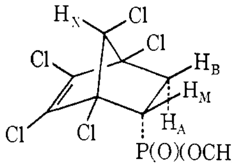
(23) Thanks are due to Dr. K. Kitahonoki from Shionogi Research Laboratories, Osaka, for a sample of this compound.

(24) C. Benezra and G. Ourisson, *Bull. Soc. Chim. Fr.*, 2270 (1966).

**Nmr Spectrum of *endo*-2-Dimethylphosphono-7-*anti*-1,4,5,6,7-pentachloro-5-bicyclo[2.2.1]heptene (8).** The gross features of the spectrum have been described elsewhere.[4a] The ABM(XY) part of the spectrum was analyzed with the LAOCN3 program, giving the following results.



$J_{AB}$ = −12.3 ± 0.03 Hz
$J_{AM}$ = 5.0 ± 0.03 Hz
$^4J_{AX}$ = 1.4 ± 0.04 Hz
$J_{AY}$ = 17.1 ± 0.05 Hz
$J_{BM}$ = 10.0 ± 0.05 Hz
$J_{BY}$ = 8.6 ± 0.05 Hz
$J_{MY}$ = −15.6 ± 0.05 Hz

$\delta_A$ 231.4 ± 0.03 Hz
$\delta_B$ 269.4 ± 0.03 Hz
$\delta_M$ 312.4 ± 0.03 Hz

***syn*-7-Bromo-*endo*-2-dimethylphosphono-*exo*-2-hydroxybicyclo[2.2.1]heptane (13).** A saturated solution of $NaOCH_3/CH_3OH$ (12 drops) was added to a mixture of *syn*-7-bromo-2-norbornanone[25] (1.404 g, 7.424 mmol) and dimethyl phosphonate (0.841 g, 76.4 mmol). After 48 hr at room temperature, the reaction mixture was chromatographed on a 50-g silica gel column. Successively eluted were (weight and eluent indicated) starting ketone (0.61 g, ether–methanol 9:1), and hydroxyphosphate **13** (1.05 g, 3.51 mmol, ether–methanol 8:2). Recrystallization from acetone afforded the analytical sample as white crystals: mp 132–133°; nmr ($CDCl_3$) 4.04 (d of m, 1 H, $H_7$, $J_{PH}$ = 5.3), 3.87 and 3.83 (2d, 6 H, nonequiv $CH_3OP$, $^3J_{PH}$ = 10.4), 3.65 (s, 1 H, OH), 2.68 and 2.54 (broad s, 2 H, $H_4$ and $H_1$), 1.30–2.39 (complex m, 6 H). Irradiation of both $H_1$ and $H_4$ causes the collapse of the d of m, at 4.04 into a d.

*Anal.* Calcd for $C_9H_{16}BrO_4P$ (299.106): C, 36.14; H, 5.39; Br, 26.72. Found: C, 36.07; H, 5.38; Br, 26.84.

Compounds **3**, **5**, **9**,[4a] **14**, **15**,[4b,c] **16**, and **17**[4b] have been described elsewhere.

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# Electrostatic Force Treatment Based on Extended Hückel Molecular Orbitals. Structure and Reaction of Simple Hydrocarbons

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**Abstract:** Taking account of the intuitiveness and usefulness of the electrostatic force (ESF) theory proposed previously, we have exploited a "semiempirical" method for calculating electrostatic Hellmann-Feynman forces based on the extended Hückel MO's. Slater exponents in the calculation of force integrals were adjusted so that the resulting forces vanished in the equilibrium structure of ethane. First, bond lengths and force constants of various hydrocarbons were calculated. Although the results seem to be generally reasonable, there still remain some difficulties to be overcome for general utility. The mechanism of the internal rotation barrier of ethane was also examined. Second, the dimerization reaction of two methyl radicals was studied. Two reaction paths were examined. One is the approach of two planar methyl radicals and the other is the approach accompanying gradual change in HCH angles of each methyl radical. It is shown that the geometrical change of the reactants along the reaction path is essential for occurrence of the reaction. If two approaching methyl radicals are restricted to be planar, the dimerization reaction cannot proceed. From the analysis of force into atomic dipole (AD), exchange (EC), and extended gross charge (EGC) forces, an intuitive understanding of the nature of both molecular structure and chemical reaction becomes possible. Some important reorganizations of electron cloud (orbital following and preceding) in the course of nuclear displacement are pointed out for both problems. From these, the usefulness of the ESF concept is confirmed in the actual calculations.

In a previous series of articles,[1] one of us presented an electrostatic force (ESF) theory in which chemical phenomena are studied using force concepts (not energetics) on the basis of the electrostatic theorem of Hellmann and Feynman.[2]

$$\mathbf{F}_A = Z_A\left[\int \rho(\mathbf{r}_1)\mathbf{r}_{A1}/r_{A1}^3\, d\mathbf{r}_1 - \sum_{B(\neq A)} Z_B\mathbf{R}_{AB}/R_{AB}^3\right] \quad (1)$$

where $\mathbf{F}_A$ is the force acting on nucleus A of a system and the other notations are the same as those in paper I. The theorem permits a classical interpretation of the force acting on a nucleus A. Namely, the force is represented by the coulombic interaction of the positively charged nucleus A with the other positively charged nuclei B and with the negatively charged electron cloud $\rho(\mathbf{r}_1)$, which may be determined by some appropriate quantum-mechanical method.[3,4] Taking advantage of this physical simplicity and visuality, we derived three pictorial forces: the atomic dipole (AD), exchange (EC), and gross charge (GC) or extended gross charge (EGC) forces. This partitioning of force was shown to be very useful in studying molecular structure and chemical reaction.[1]

On the other hand, the calculations of electrostatic forces have been reported by several investigators.

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[3] A. C. Hurley, "Molecular Orbitals in Chemistry, Physics and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., p 161; *Proc. Roy. Soc., Ser. A*, **226**, 170, 179 (1954).

[4] G. G. Hall, *Phil. Mag.*, **6**, 249 (1961).