suspension was cooled (salt–ice bath) and then methyl methylsulfinylmethyl sulfide[32,33] (11.3 g, 0.091 mol) was added dropwise. After the mixture was stirred for 1 h, 1,4-dibromobutane-*2,2,3,3-d*$_4$ (20.0 g, 0.091 mol) was added dropwise. The mixture was stirred for 1.5 h with cooling and 20 h at room temperature and then quenched by adding 6 mL of 25% NH_4Cl. The mixture was filtered and evaporated and then taken up in 150 mL of diethyl ether, and 0.4 mL of 9 N sulfuric acid was added. The solution was stirred for 30 h and then poured into 20 mL of saturated $NaHCO_3$ solution. The aqueous phase was washed with diethyl ether (3 × 10 mL). The combined ethereal solutions were dried ($MgSO_4$), filtered, and evaporated to ca. 25 mL. The solution was stirred with a saturated solution of 15 g of $NaHSO_3$ for 30 min. The aqueous layer was removed and the ether phase stirred with a saturated solution of 5 g of $NaHSO_3$ for 30 min. The combined aqueous phases were treated with 20% NaOH (50 mL) and extracted with diethyl ether. The combined ether extracts were dried ($MgSO_4$), filtered, and evaporated to give 4.45 g of cyclopentanone-*3,3,4,4-d*$_4$ (56%). ^{13}C NMR ($CDCl_3$) 220.0, 37.7, 21.9 ppm (5 lines, J_{CD} = 20 Hz).

Cyclopentanone-*2,2,3,3,4,4,5,5-d*$_8$. A mixture of cyclopentanone-*3,3,4,4-d*$_4$ (4.0 g), D_2O (25 mL), and K_2CO_3 (0.4 g) was stirred for 19 h. The mixture was extracted with diethyl ether (4 × 10 mL). The combined ether extracts were evaporated and the exchange repeated as above. Workup as above followed by distillation (bp 126–129 °C) gave 1.80 g of a clear liquid. ^{13}C NMR ($CDCl_3$) 220.2, 37.1 (p, J_{CD} = 20 Hz), 21.7 ppm (p, J_{CD} = 20 Hz).

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Registry No. 2, 51804-49-0; **3**, 17106-22-8; 1,4-dibromobutane-*2,2,3,3-d*$_4$, 52089-63-1; cyclopentanone-*3,3,4,4-d*$_4$, 36219-23-5; cyclopentanone-*2,2,3,3,4,4,5,5-d*$_8$, 4477-17-2.

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Cation Effects on One Bond P–H Coupling Constants in Phosphinate Ion (Hypophosphite Ion). Experimental Evidence for the Effect of Association with Metal Cations on the Structure of Tetracoordinate Phosphorus Anions in Solution

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Abstract: In order to test the proposal that metal ion association affects bond angles in phosphate anions, the effect of metal ions on the one bond P–H coupling constant, $^1J_{PH}$, in phosphinate ion (hypophosphite ion), $H_2PO_2^-$, has been observed by studying couplings over a range of metal ion concentrations and extrapolating to complete association. Ions with small ionic radii, Li^+, Mg^{2+}, and Zn^{2+}, have large effects, increasing $^1J_{PH}$ by 14, 18, and 26 Hz (Table I). Ba^{2+} has a small effect on $^1J_{PH}$, and Sr^{2+} and Ca^{2+} have successively larger effects. Guanidinium ion has almost no effect. The pattern of these effects is consistent with increases in $^1J_{PH}$ due to bidentate coordination causing a decrease in the O–P–O bond angle. The result for Li^+ indicates inner sphere coordination.

The association of cations with phosphate anions appears to have important functional consequences in binding to enzymes, enzymic catalysis, nucleic acids, and expression of genetic information.[1-3] The structural effect on phosphates due to association with cations could be significant. On the basis of ^{31}P NMR chemical shifts,[4-8] it has been proposed that the O–P–O bond angle in phosphate anions is altered by the presence of small divalent metal cations due to electrostatic attractive forces. In this paper, we report experimental results which give information about the effects on O–P–O bond angles due to complexation with metal ions. The experimental method utilizes one bond P–H coupling constants ($^1J_{PH}$) for $H_2PO_2^-$.

Moedritzer et al.[5] reported the ^{31}P NMR spectra of over 200 phosphorus compounds including a few one bond P–H couplings. Van Wazer et al. studied the chemical shifts of phosphate esters and interpreted the results in terms of a quantum mechanically derived relationship which involved the electronegativity of the phosphoryl oxygens, the degree of occupation of the d-orbitals, and the O–P–O bond angle.[6] Gorenstein,[7,8] after examining the ^{31}P chemical shifts of various phosphate esters, proposed an empirical correlation between O–P–O bond angles and ^{31}P chemical shifts. Citing disagreement between his data and Van Wazer's approach, he has concluded that the effects of d-orbital participation and phosphoryl oxygen electronegativity are minor. Prigodich used ^{31}P NMR chemical shifts (relative to trimethylphosphate as a standard) to determine association constants of various mono- and dications with mono- and dianion phosphate esters.[4] The association of small metal dications causes upfield chemical shifts in phosphate ester anions consistent with decreases in the O–P–O bond angle whereas monocations and large dications cause downfield chemical shifts consistent with predominance of electrostatic deshielding.

Hypophosphite anion ($H_2PO_2^-$) is structurally similar to a phosphate anion but contains two P–H bonds. As is true for C–H couplings, the $^1J_{PH}$ is predominantly sensitive to the hybridization of the P–H bond.[9] If the O–P–O angle decreases due to bidentate coordination to a metal ion, the p-orbital contribution from phosphorus in the P–O σ bonds will increase. This will cause increased s-orbital contribution from phosphorus in the P–H bonds

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Table I. ΔJ_{max}'s and Equilibrium Constants[a]

cation	ΔJ_{max} (Hz)	J_c (Hz)[b]	K (M^{-1})	ionic radius[25] (Å)
		518.4		
3 M $(H_2N)_3C^+$		518.9		
Zn^{2+}	26 (2)	544	1.3 (2)	0.74
Cd^{2+}	19 (3)	537	1.5 (6)	0.97
Mg^{2+}	18 (2)	536	0.9 (1)	0.65
Li^+	14 (3)	532	0.15 (5)	0.60
Ca^{2+}	9.7 (6)	528.1	1.1 (2)	0.99
Sr^{2+}	7.0 (5)	525.4	0.9 (1)	1.15
Na^+	3.1 (3)	521.5	0.20 (5)	0.95
Ba^{2+}	4.5 (7)	522.9	0.9 (4)	1.35
Mg^{2+}[c]	20 (1)	538	0.73 (5)	0.65

[a] Calculated from eq 1; standard deviations in parentheses. [b] Obtained by the addition of the calculated ΔJ_{max} and the $^1J_{PH}$ of the free hypophosphite anion, 518.4 Hz. [c] Constant [Cl^-] maintained with guanidinium chloride.

and a larger P–H coupling constant. One such experiment has been reported: Zn^{2+} increased $^1J_{PH}$ in $H_2PO_2^-$.[10]

Experimental Section

Stock solutions which contained the cation chlorides (Reagent grade) in H_2O were combined with a stock solution of 0.2 M hypophosphorous acid in H_2O and diluted in order to obtain samples of varying cation chloride concentrations and constant (0.02 M) hypophosphite concentration. For one set of spectra, solutions containing Mg^{2+} were made at constant [Cl^-] maintained by guanidinium chloride, $C(NH_2)_3Cl$ (recrystallized). The resulting solutions were approximately 40% ^2H_2O in order to obtain a deuterium lock for the NMR spectrometer.

The pH of the solutions was adjusted with tetramethylammonium hydroxide and 3 N HCl and the solutions were made CO_2 free by bubbling N_2 through them. The digital recording of the phosphorus-31 NMR coupling constants was done on a Varian XL-200 spectrometer at 21 (1) °C. Measurements are accurate within 0.1 Hz.

Results

Coupling constants as a function of cation concentration demonstrate that $^1J_{PH}$ is dependent on the type of cation and the cation concentration. Since exchange is fast for these ions, $^1J_{PH}$ represents a time-weighted average of coupling constants for the complexed and uncomplexed forms of the hypophosphite anion. We analyzed our data (see supplementary material) by using the mathematical treatment presented earlier.[4] Using $^1J_{PH}$ as the experimental probe, eq 1 results (the derivation is given by Prigodich[4])

$$1/\Delta J_{obsd} = (1/K\Delta J_{max}[M]) + (1/\Delta J_{max}) \qquad (1)$$

where ΔJ_{obsd} is the change in $^1J_{PH}$ relative to the free hypophosphite ion, ΔJ_{max} is the maximum change in $^1J_{PH}$ due to association of the cation, K is the association constant, and [M] is the cation concentration. Equation 1 is based on approximating the free metal ion concentration [M] as the total metal ion concentration since [$H_2PO_2^-$] is low relative to [M]. This double reciprocal treatment of our data gave straight lines, and by least-squares analysis yielded ΔJ_{max} which represents the change in the $^1J_{PH}$ caused by $H_2PO_2^-$ fully complexed to the cation relative to free hypophosphite. Table I presents the calculated ΔJ_{max}'s, K's, and J_c's for full complexation to the cations based on eq 1. The values in parentheses are standard deviations. One sees a clear correlation of the magnitude of ΔJ_{max} with ionic radius. The ions with the largest effects, Zn^{2+} and Mg^{2+}, are dications with the smallest ionic radii. The comparison of the effects of Li^+ with Sr^{2+} and Ba^{2+} shows that a small ionic radius has a greater effect on ΔJ_{max} than changing from a monocation to a dication. Almost no effect is observed with guanidinium ion.

We also observed couplings in $HDPO_2^-$ and $D_2PO_2^-$ as a result of acid-catalyzed deuterium exchange of hypophosphorous acid in D_2SO_4 and D_2O. $HDPO_2^-$ causes a doublet of triplets and $D_2PO_2^-$ causes a quintet pattern. The $^1J_{PH}$ and $^1J_{PD}$ of the unprotonated, singly protonated, and doubly protonated species are reported in Table II. $^1J_{PD}$'s are smaller than the respective $^1J_{PH}$ values but they correlate with increases and decreases in $^1J_{PH}$. This can be seen by comparing the changes in $^1J_{PH}$ and $^1J_{PD}$ caused by protonation of hypophosphorous acid. The increase in $^1J_{PH}$ of 106.7 Hz represents an 18.8% change which is equivalent to the 18.8% increase (16.7 Hz) in the $^1J_{PD}$. Mg^{2+} increases the coupling constants proportionately, and guanidinium ion has no effect on either $^1J_{PH}$ or $^1J_{PD}$ in $HDPO_2^-$. The ratio of $^1J_{PH}$:$^1J_{PD}$ is 6.51.

Table II. $^1J_{PD}$ and $^1J_{PH}$ Results for Acid Species[a]

species	$^1J_{PH}$	$^1J_{PD}$
$H_2PO_2^-$	518.4	
$HDPO_2^-$	517.5	79.5
$HDPO_2^-$ in 1 M $MgCl_2$	526.5	80.9
$H_2P(O)OD$	566.9	
$HDP(O)OD$	566.6	86.7
$D_2P(O)OD$		86.8
$H_2P(OD)_2^+$	673.5	
$HDP(OD)_2^+$	673.3	103.0
$D_2P(OD)_2^+$		102.8

[a] The coupling constants are in Hz.

Discussion

In one bond couplings, the Fermi contact terms are dominant:[9] an increase in the s-orbital participation in the bond will result in an increase in the one bond coupling constant. A great deal of research has demonstrated that C–H couplings depend predominantly on percent s-orbital character in bonding at carbon.[9,11-13]

This same correlation with s character at phosphorus appears dominant in one bond P–H couplings:[14-19] phosphines have couplings near 200 Hz consistent with a small bond angle (93.6° in PH_3) and, therefore, predominant p-orbital contribution to bonding; in contrast, phosphonium ion, $^+PH_4$, gives $^1J_{PH} = 547$ Hz with tetrahedral bonding and 25% s character at phosphorus.[18,20]

Beer and Grinter[16] have proposed that other spin–spin mechanisms are important in the $^1J_{PX}$ of trivalent compounds, and McFarlane[17] has observed a dependence of the $^1J_{PX}$ of various protonated phosphines on the effective nuclear charge of phosphorus. Nevertheless, for tetracoordinate phosphorus compounds, experimental results and theoretical calculations based on the Fermi contact mechanism have led to the conclusion that it is *primarily* s character which determines $^1J_{PH}$.[14]

Sheldrick[19] has observed an increase in the $^1J_{PH}$ of phosphine (PH_3), hypophosphorus acid (H_2PO_2H), and orthophosphorus acid (HPO_3H_2) upon protonation in strong acid. Moedritzer[21] has studied the pH dependence of the $^1J_{PH}$ of the hypophosphite anion and hypophosphorus acid and used these values to determine the acidity constants (pK_a's) of the acid. He observed an increase in $^1J_{PH}$ with decreasing pH. Haas and Gillman[10] further studied this dependence and also determined the Zn^{2+} association constant by observing increases in the $^1J_{PH}$ due to Zn^{2+} association. Fitch[22] has reported the $^1J_{PH}$ of methyl hypophosphite ester (517 Hz), ethyl hypophosphite ester (567 Hz), and butyl hypophosphite ester (570 Hz).[23]

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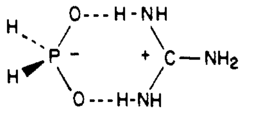
Sources of Changes in $^1J_{PH}$. Two factors need to be considered in understanding the effects of Table I. First, metal ion association could polarize the electron clouds around the oxygen atoms thereby drawing more p character at phosphorus into the P–O σ bonds. Second, decrease in the O–P–O bond angle due to bidentate coordination to metal ions would cause more p-orbital contribution (due to a smaller interorbital angle between p functions) at phosphorus in the P–O bonds. Either effect would cause more s character in the P–H bonds and increased $^1J_{PH}$ values.

The results in Table I indicate that ΔJ_{max} correlates very strongly with ionic radii. In addition, guanidinium ion ($C(NH_2)_3^+$) should associate to the hypophosphite anion through a cyclic hydrogen bonded complex with two hydrogen bonds, **1**, which requires no change in the O–P–O bond angle for effective hydrogen bonding. We previously have published several determinations of the association constant for guanidinium ion and phosphate monoanions.[4,24] These data suggest $K \doteqdot 0.2\ M^{-1}$ should be reasonable. Therefore, at 3 M guanidinium ion, the ratio of complexed $H_2PO_2^-$ to free $H_2PO_2^-$ should be 0.6. The results in Table I indicate a very small effect of association of guanidinium ion on $^1J_{PH}$. This result plus the small Ba^{2+} effects on ΔJ_{max} are in marked contrast to the large effects due to the ions with small ionic radii. Therefore, there is clear evidence that bond angle effects are the most important factor in changing J_{PH}.



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Comparison of the magnitude of the metal ion effects in Table I also indicates qualitatively that the predominant effect on $^1J_{PH}$ is due to changes in O–P–O bond angle. For Ba^{2+}, with a large ionic radius, bidentate coordination is possible with little or no change in O–P–O bond angle; consistent with this prediction, the $^1J_{PH}$ at 1.0 M concentration is 2.3 Hz and ΔJ_{max} is 4.5 Hz; these values are small compared to the increases in $^1J_{PH}$ at 1.0 M concentration for Mg^{2+} (8.9 Hz) and Zn^{2+} (15.8 Hz) and the ΔJ_{max}'s for Mg^{2+} (18 Hz) and Zn^{2+} (26 Hz). These results are not consistent with electrostatic effects alone because Mg^{2+} and Ba^{2+} are both dications and should give similar increases in $^1J_{PH}$. Furthermore, the increases in $^1J_{PH}$ due to Li^+ at 3.6 M concentration (5.7 Hz) and ΔJ_{max} (14 Hz) are significantly greater than those of Ba^{2+}; electrostatic reasoning would predict a larger effect from Ba^{2+} (a dication) than from Li^+ (a monocation). One would, therefore, expect smaller increases in the $^1J_{PH}$ for Li^+ as opposed to Ba^{2+}, which is contradictory to our results: ΔJ_{max} is 14 for Li^+ and 4.5 for Ba^{2+}.

The large effects caused by Li^+, Mg^{2+}, and Zn^{2+} are consistent with decreases in the O–P–O bond angle as a result of Coulombic attractive forces in the chelated, associated species. The cations which engender the largest effects on $^1J_{PH}$ have the smallest ionic radii, Li^+ (0.60 Å), Mg^{2+} (0.65 Å), and Zn^{2+} (0.74 Å),[25] consistent with contraction of the O–P–O angle; however, the ΔJ_{max} values of the alkaline earth metal ions, Ca^{2+}, Sr^{2+}, and Ba^{2+}, cause successively less effect on the P–H coupling as the ionic radius increases. Similarly, Li^+ (radius 0.60 Å) has a much larger effect than Na^+ (radius 0.95 Å). It is clear from this result that Li^+ must have an inner sphere interaction with $H_2PO_2^-$; Li^+ may also have more covalent bonding to $H_2PO_2^-$ than the other cations.

Mg^{2+} and Zn^{2+} have similar ionic radii, but Zn^{2+} causes a larger increase in $^1J_{PH}$ than Mg^{2+}. This can be understood from the difference in effective nuclear charge: Zn^{2+} contains 10 d-electrons which do not completely shield the nucleus, so its effective nuclear charge (Z_{eff}) at the empty 4s-orbital is 4.7 as opposed to 3.2 for the empty 3s-orbital of Mg^{2+}.[26] Thus, the hypophosphite ion will see a greater positive charge and have greater electrostatic interaction when associated to Zn^{2+} as compared to Mg^{2+}. This is consistent with the results in Table I. Similarly Cd^{2+} gives a larger ΔJ than Ca^{2+} despite the similarity in ionic radii.

Therefore, bond angle effects appear dominant in these $^1J_{PH}$ values. The contrast with the complexity of effects on ^{31}P chemical shifts suggests that $^1J_{PH}$ is a more direct way to study perturbations of tetracoordinate phosphorus anion structure.

The electrostatic energy of interaction can be calculated from $E = NZ_1Z_2e^2/Dr$.[24] In order to estimate energies, due to bidentate coordination, we have to sum two interactions between the cation and the two oxygens of $H_2PO_2^-$. The radius, r, is the sum of ionic radii: for the oxygens we use 1.76 Å as the ionic radius, and the cation radii are in Table I.[25] In such electrostatic calculations, the dielectric constant is a major problem.[27,28] Following the work of Orttung, we use $D = 2$ for the dielectric between the ions.[28] Then, the electrostatic energy of interaction is 70 kcal/mol for Li^+ and 137 kcal/mol for Mg^{2+}. Solvation effects would decrease this, but despite the uncertainties in dielectric constant and solvation effects, these numbers are clearly large enough to force changes in the O–P–O bond angle. It is very likely that the bond angles change more than the interorbital angles in $H_2PO_2^-$ so that the observed ΔJ_{max} values are less than would be expected from bond angle effects. In addition, although the results seem consistent with changes in bond angle, electrostatically caused polarization of electron distribution must have some effect on ΔJ. Therefore, ΔJ_{max} cannot be used quantitatively to get an experimental value for the effect of bidentate coordination on bond angle. When covalent bonds are formed, bond angle effects are larger: for example, $R_2XO_2PH_2$ compounds,[29] with X = Al, Ga, and In, give larger $^1J_{PH}$ values than we observed here for ionic interactions.

Association Constants. The application of eq 1 to our data yields association constants which are less than those we found for dimethyl phosphate monoanion of about 3 M^{-1}.[4] Haas and Gillman,[10] utilizing $^1J_{PH}$'s, have reported K's of 3.5 (5) M^{-1} and 2.0 (5) M^{-1} for the association of Zn^{2+} to $H_2PO_2^-$. In the latter investigation a constant ionic strength was maintained with sodium perchlorate or sodium nitrate, respectively. Prigodich used a medium with constant chloride ion maintained with $N(CH_3)_4Cl$.[4] As a result of the data in Table I, we felt that the addition of $NaClO_4$ or $NaNO_3$ could not only affect the J_{obsd} by introducing sodium ion into the sample but also that the ClO_4^- or NO_3^- could associate with the cation under study and affect the equilibrium. In fact, the higher K's observed previously could be due to competition for Zn^{2+} ion by NO_3^- and ClO_4^-. An alternative, frequently used method, the addition of $N(CH_3)_4Cl$, clearly would perturb the $^1J_{PH}$ significantly since we found that at 3.0 M $N(CH_3)_4Cl$, $\Delta J = -6.6$ Hz.[30] Therefore, no compensation was made for ionic strength or [Cl^-]. In order to determine the effect of [Cl^-] on ΔJ and calculated K's, we made an additional determination of the Mg^{2+} effect at constant [Cl^-] maintained with guanidinium chloride, $C(NH_2)_3Cl$. This salt was chosen because $C(NH_2)_3Cl$ had been found (Table I and supplementary material) to cause only a minor effect on the $^1J_{PH}$ (ΔJ at 3.0 M = 0.5 Hz). No significant differences between the $^1J_{PH}$ of the constant [Cl^-] and original runs were observed (Table I).

The two results for Mg^{2+} and the consistency in our K values (Table I) appear to indicate that these K's are valid for bidentate coordination to $H_2PO_2^-$ under the experimental conditions. Of course, other geometries of interaction are possible, but we will only detect the chelated modes of ionic bonding if that effect on $^1J_{PH}$ is dominant.

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Registry No. $H_2PO_2^-$, 15460-68-1; Zn, 7440-66-6; Cd, 7440-43-9; Mg, 7439-95-4; Li, 7439-93-2; Ca, 7440-70-2; Sr, 7440-24-6; Na, 7440-23-5; Ba, 7440-39-3.

Supplementary Material Available: Original data on $^1J_{PH}$ and $^1J_{PD}$ (4 pages). Ordering information can be found on any current masthead page.

Valence Isomerization of the Radical Cations of Bicyclopentanes in γ-Irradiated Low-Temperature Freon Matrices

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Abstract: The radical cation of spiro[2.2]pentane was produced in a γ-irradiated CCl_3F matrix at 4 K. Analysis of the observed ESR spectrum has led, by a process of elimination, to the conclusion that the radical cation is probably Jahn-Teller (J-T) distorted from D_{2d} to C_{2v}. At 77 K the distorted radical cation isomerizes to the radical cation of methylene cyclobutane. Above 77 K the latter shows a reversible ESR spectral change which may be interpreted in terms of the isomerization to a nonclassical radical cation. The radical cation of bicyclo[2.1.0]pentane isomerizes even at 4 K to the radical cation of cyclopentane. The results are discussed in comparison with ab initio MO calculations.

In view of the recent studies of the ring opening of the radical cations of cyclopropane and its derivatives under particular experimental conditions,[1] it seemed interesting to extend the study to bicyclic hydrocarbons bearing the cyclopropyl ring. Two examples of such systems, spiro[2.2]pentane and bicyclo[2.1.0]pentane, were studied in the present work by the Freon matrix technique originally proposed by one of the present authors.[2,3] The homolysis of the neutral radicals derived by hydrogen abstraction from these pentanes has been reported previously.[4]

We have obtained an ESR spectrum for the radical cation of spiropentane in the Freon matrix at 4 K which is not incompatible with the assumption that the radical cation is J-T distorted from D_{2d} to C_{2v}. The distorted radical cation suffers a ring opening at 77 K to isomerize to the radical cation of methylenecyclobutane. The ESR spectrum of the latter changes reversibly between 77 K and ~150 K which may indicate the occurrence of a nonclassical radical cation.

As for the radical cation of bicyclo[2.1.0]pentane, it isomerizes to the radical cation of cyclopentane even at 4 K. The observed results have been substantiated by ab initio UHF MO calculations with the STO-3G and 4-31G basis sets.

Experimental and Computational

The two bicyclopentanes were prepared by the method in the literature.[4] Each of the hydrocarbons was dissolved in CCl_3F with concentrations of 0.2-0.5 mol % and γ-irradiated in a Suprasil ESR cell at 4 K, 77 K, and various temperatures up to ~150 K. The general description of the Freon matrix technique to obtain the solute radical cations has been described elsewhere.[2,3,5]

The optimum geometries of the various isomers were calculated by the GRADIENT method incorporated in the Gaussian 80 program with the approximation of UHF and the STO-3G and 4-31G basis sets.

Results and Discussion

(1) The Radical Cation of Spiro[2.2]pentane at 4 K. As in the case of allene the radical cation of spiropentane should be distorted from D_{2d} to either D_2 or C_{2v} by the J-T effect.[6] In both cases the total eight protons will be divided into two groups of four positionally equivalent protons (see the bottom of Figure 1). According to the following reasoning (i-iii), the possibility of the D_2 deformation is eliminated and that of C_{2v} is favored.

(i) Geometry Optimization with the Symmetry Restrictions of D_2 and C_{2v}. The result obtained with the 4-31G basis set is illustrated in Figure 1. The total energies were −193.3152 and −193.3249 hartrees for D_2 and C_{2v}, respectively. In the D_2 conformation the two cyclopropyl rings assume acute isosceles triangles, with an angle of 54.6° between the planes of the rings. In the C_{2v} conformation both rings have obtuse isosceles structures, but the two upper methylene groups of Figure 1 are almost in an sp^2-hybridized state. The deformations are understandable as follows. In the D_2 conformation the highest singly occupied MO (see the bottom of Figure 1) is related to the antisymmetric component of the degenerate HOMO (3e′) of cyclopropane.[7-9] Since this component is characterized as bonding between the central and the methylene carbon atoms, the depletion of one electron from the HOMO of the parent molecule should stretch the bonds as found. Likewise, we can consider that in the C_{2v} conformation one electron has been lost from the symmetric component of the degenerate HOMO of one of the two orthogonal cyclopropane rings, which should weaken the C-C bond between the two adjacent methylene groups. Unlike the D_2 conformation the odd electron is found localized mostly in one of the cyclopropyl units, causing the remarkable bond stretching in one of the two

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