(47) The average is calculated as $\bar{x} = (\Sigma x_i)/n$ and the standard deviation is $\sigma(\bar{x}) = [\Sigma x_i - x)^2/n]^{1/2}$.

(48) The standard deviation of the difference is given as $\sigma(\text{difference}) = (\sigma_1^2 + \sigma_2^2)^{1/2}$.

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# Geometry of Cycloheptane Conformers. Crystal Structure of 1-Dimethylphosphono-1-hydroxycycloheptane[1]

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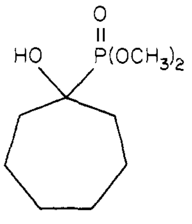
*Received April 18, 1977*

**Abstract:** In order to establish the conformation of 1-dimethylphosphono-1-hydroxycycloheptane (**1**) in the solid state we carried out an x-ray analysis. Crystals of **1** belong to the triclinic space group $P\bar{1}$ with cell dimensions $a$ = 8.443, $b$ = 11.346, $c$ = 6.785 Å; $\alpha$ = 101.30, $\beta$ = 111.21, $\gamma$ = 98.41°. Intensity data were measured on a diffractometer with Mo radiation. The structure was solved by direct methods and refined by block-diagonal least squares. The final agreement index $R$ is 0.045 for 2351 reflections. A difference Fourier map revealed that two atoms in the cycloheptane ring, C(6) and C(7), are disordered, each of them occupying two distinct positions. Consequently, both the twist-chair and the chair conformers occur in the crystal structure; their relative abundance, as determined by a refinement of occupancy factors, is 0.93 and 0.07. In the twist-chair the two substituents occupy isoclinal positions at C(1), while in the chair conformer the dimethylphosphonate group is equatorially oriented. Bond angles and torsion angles in the twist-chair conformer agree very well with those calculated with Allinger's force field. The chair form agrees best with the model obtained from Boyd's field. The ratio of the two conformers corresponds to $\Delta E$ = 1.5 kcal/mol. From this one can calculate that moving a hydroxyl group from an isoclinal to an axial position at C(1) raises the energy by 0.5 kcal/mol.

Recent efforts in one of these laboratories have been directed toward a clarification of geometries of medium-ring compounds, using $^{13}C$ NMR spectroscopy.[3,4] In the course of examining a series of cyclic hydroxyphosphono compounds, it became apparent that x-ray data for the cycloheptane derivative would be desirable in view of apparent anomalies between the expected geometry and the observed $^{13}C\text{-}C\text{-}C\text{-}^{31}P$ coupling constants. Experimental information about the conformation of cycloheptane rings is rather limited.[5] Many crystal structures have been determined in which seven-membered rings are fused to others[6] and such results have been used to discuss the conformation of these rings.[7,8] However, when we started this study we were aware of only one published x-ray analysis of a compound containing an isolated cycloheptane ring.[9a] For various reasons, including extensive disorder and the presence of a bromine atom, the precision of that structure analysis was rather low. Consequently, it appeared worthwhile to determine the crystal structure of 1-dimethylphosphono-1-hydroxycycloheptane (**1**). Very recently, after our work was completed, the structure of calcium cycloheptane carboxylate pentahydrate was published.[9b] Owing to pseudorotation all ring atoms were found to be disordered and it was not possible to obtain precise results.



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## Experimental Section

Colorless crystals of **1** were obtained from ethyl acetate (mp 106.0–107.5 °C). Precession photographs indicated triclinic symmetry; in the absence of chiral centers the space group was expected, and later confirmed, to be $P1$. A crystal fragment measuring 0.5 × 0.5 × 0.5 mm was mounted along the $a^*$ axis on a card-controlled Picker four-circle diffractometer. Cell dimensions were determined from angular settings of 15 high-angle reflections and both Cu K$\alpha_1$ ($\lambda$ 1.54051 Å) and Cu K$\alpha_2$ ($\lambda$ 1.54433 Å) radiations were used. The following crystal data were obtained: $a$ = 8.443 (1), $b$ = 11.346 (1), $c$ = 6.785 (1) Å; $\alpha$ = 101.30 (2), $\beta$ = 111.21 (2), $\gamma$ = 98.41 (2)°; $V$ = 577.2 Å$^3$; $D_x$ = 1.28 g cm$^{-3}$; $Z$ = 2; $F(000)$ = 240; $\mu$(Mo K$\alpha$) = 2.20 cm$^{-1}$.

Table I. Final Parameters and Their Standard Deviations

A. Anisotropic Atoms[a]

| Atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| P | 7011.9 (6) | 3463.2 (4) | 5646.9 (8) | 349 (2) | 318 (2) | 435 (2) | 116 (2) | 159 (2) | 91 (1) |
| O(1) | 3933 (2) | 3331 (1) | 5623 (2) | 540 (7) | 512 (7) | 565 (7) | 228 (6) | 324 (6) | 231 (6) |
| O(2) | 7420 (2) | 4772 (1) | 5697 (3) | 523 (7) | 376 (6) | 732 (9) | 174 (6) | 275 (7) | 104 (5) |
| O(3) | 7881 (2) | 2621 (1) | 4437 (3) | 434 (7) | 484 (7) | 773 (9) | 58 (7) | 282 (7) | 124 (5) |
| O(4) | 7687 (2) | 3244 (1) | 7992 (2) | 613 (8) | 603 (8) | 512 (8) | 218 (7) | 73 (6) | 87 (7) |
| C(1) | 4683 (2) | 2697 (1) | 4272 (3) | 378 (7) | 359 (7) | 396 (8) | 138 (6) | 164 (6) | 117 (6) |
| C(2) | 4414 (2) | 1352 (1) | 4387 (3) | 407 (8) | 363 (8) | 472 (9) | 172 (7) | 141 (7) | 107 (6) |
| C(3) | 2591 (2) | 529 (2) | 2939 (3) | 381 (8) | 418 (8) | 556 (10) | 176 (7) | 182 (7) | 90 (6) |
| C(4) | 2380 (3) | −92 (2) | 649 (4) | 486 (10) | 475 (10) | 622 (12) | 6 (9) | 175 (9) | 77 (8) |
| C(5) | 2381 (3) | 741 (2) | −829 (4) | 599 (12) | 741 (14) | 413 (10) | −14 (9) | 177 (9) | 42 (10) |
| C(6) | 3898 (3) | 1895 (2) | 101 (4) | 551 (12) | 689 (14) | 452 (10) | 148 (9) | 269 (9) | 165 (10) |
| C(7) | 3871 (3) | 2863 (2) | 1962 (3) | 476 (9) | 474 (9) | 422 (9) | 195 (8) | 186 (8) | 178 (8) |
| C(8) | 9747 (3) | 2895 (3) | 5075 (5) | 442 (10) | 700 (14) | 1011 (19) | 140 (13) | 336 (12) | 182 (10) |
| C(9) | 7781 (5) | 4132 (3) | 9872 (4) | 923 (20) | 982 (21) | 450 (12) | 99 (12) | 218 (12) | −60 (16) |

B. Isotropic Atoms[b]

| Atom | $x$ | $y$ | $z$ | $U$ | Atom | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|---|---|---|---|---|
| C(6′) | 258 (3) | 219 (2) | 8 (4) | 42 (5) | H(62) | 384 (4) | 229 (3) | −115 (5) | 73 (9) |
| C(7′) | 449 (3) | 266 (2) | 165 (4) | 41 (5) | H(71) | 264 (4) | 286 (3) | 157 (5) | 72 (9) |
| H(21) | 520 (3) | 101 (2) | 394 (4) | 43 (5) | H(72) | 436 (3) | 364 (2) | 200 (4) | 47 (6) |
| H(22) | 466 (4) | 135 (3) | 591 (5) | 58 (6) | H(81) | 1018 (7) | 279 (5) | 636 (9) | 134 (16) |
| H(31) | 240 (4) | −8 (3) | 363 (5) | 57 (6) | H(82) | 1011 (6) | 365 (4) | 504 (7) | 100 (11) |
| H(32) | 176 (3) | 97 (2) | 286 (4) | 44 (5) | H(83) | 998 (7) | 245 (5) | 398 (8) | 122 (15) |
| H(41) | 143 (4) | −67 (3) | −5 (6) | 76 (9) | H(91) | 839 (8) | 397 (5) | 1092 (10) | 137 (17) |
| H(42) | 335 (4) | −52 (3) | 79 (5) | 63 (8) | H(92) | 821 (6) | 498 (4) | 977 (8) | 111 (14) |
| H(51) | 129 (4) | 104 (3) | −125 (5) | 66 (8) | H(93) | 674 (9) | 398 (6) | 993 (11) | 158 (22) |
| H(52) | 227 (5) | 26 (4) | −218 (6) | 89 (10) | H(O1) | 357 (3) | 393 (2) | 513 (4) | 42 (5) |
| H(61) | 503 (5) | 169 (3) | 59 (6) | 76 (9) | | | | | |

[a] All parameters were multiplied by $10^4$. The thermal parameters are expressed as $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^* + \cdots)]$. [b] All parameters were multiplied by $10^3$.

Table II. Torsion Angles (Degrees) in the Twist-Chair and Chair Conformers[a]

| | | |
|---|---|---|
| C(1)-C(2)-C(3)-C(4) | +88.6 | +88.6 |
| C(2)-C(3)-C(4)-C(5) | −69.8 | −69.8 |
| C(3)-C(4)-C(5)-C(6) | +50.8 | −1 |
| C(4)-C(5)-C(6)-C(7) | −68.6 | +73 |
| C(5)-C(6)-C(7)-C(1) | +84.5 | −95 |
| C(6)-C(7)-C(1)-C(2) | −35.7 | +74 |
| C(7)-C(1)-C(2)-C(3) | −42.0 | −65 |
| P(1)-C(1)-C(2)-C(3) | −168.7 | −168.7 |
| P(1)-C(1)-C(7)-C(6) | +90.0 | −173 |

[a] The values in the second column (chair conformer) were calculated by substituting C(6′) and C(7′) for C(6) and C(7).

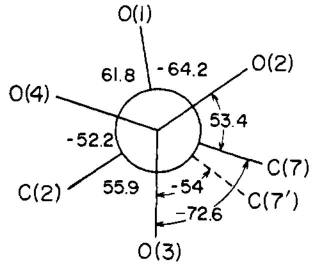

Figure 1. Newman projection along the P–C(1) bond. The conformation in the chair conformer is indicated by the dashed line.

Intensity data were measured with niobium-filtered molybdenum radiation by the use of the moving-crystal/moving-counter technique ($\theta$-$2\theta$ scan). A net count of 100 or 10% of the background, whichever was higher, was determined as threshold intensity below which reflections were considered unobserved. There were 2632 unique reflections with $2\theta \leq 55°$ of which 2310 (88%) had intensities above threshold values. The intensities were corrected for Lorentz and polarization factors; absorption corrections were considered unnecessary in view of the low value of $\mu$ and the regular shape of the crystal.

The structure was determined by the symbolic addition procedure.[10] Atomic parameters were refined by block-diagonal least squares. All hydrogen atoms were located on difference Fourier maps and their parameters were refined isotropically. Scattering factors were taken from the "International Tables for X-Ray Crystallography".[11] Throughout the refinement the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized and a factor of 0.8 was applied to all shifts. The following weighting scheme was used during the final stages: $w = w_1w_2$, where $w_1 = 5/|F_o|$ for $|F_o| > 5$, $w_1 = |F_o|/5$ for $|F_o| \leq 5$; and $w_2 = \sin^2\theta/0.12$ for $\sin^2\theta < 0.12$, $w_2 = 1$ for $\sin^2\theta \geq 0.12$. The refinement was assumed to be finished when the average parameter shift equalled $0.1\sigma$ and the largest one $0.5\sigma$. At this stage the agreement index $R(\Sigma|\Delta F|/\Sigma|F_o|)$ was 0.049 and the weighted index $R'$ $(\Sigma w\Delta F^2/\Sigma wF_o^2)$ was 0.055 for 2348 reflections, including 38 unobserved ones for which $|F_o| < |F_c|$. However, a difference Fourier map revealed two small peaks (0.55 and 0.37 e$\AA^{-3}$) which were found to correspond to alternate sites for C(6) and C(7). Refinement was therefore continued and included C(6′) and C(7′) with isotropic temperature parameters as well as occupancy factors for C(6), C(7), C(6′), and C(7′). These factors converged at the following values: 0.91 (1) and 0.96 (1) for C(6) and C(7); 0.09 (1) and 0.06 (1) for C(6′) and C(7′), respectively. In the final two cycles the occupancy factors were fixed at 0.93 for the major sites and 0.07 for the minor sites. At the end of the refinement the average parameter shift equalled $0.05\sigma$ and the maximum $0.57\sigma$. $R$ and $R'$ decreased significantly: their final values are 0.045 and 0.051, respectively, for 2351 reflections. The final difference Fourier map no longer had the peaks mentioned earlier. It was featureless except for two small peaks, seen also on the previous map, located on midpoints of the C(1)-P and C(1)-C(2) bonds.

## Results and Discussion

The final coordinates and temperature parameters, as well as their standard deviations, are listed in Table I. The conformation of the major and minor conformers can be assessed on the basis of the torsion angles given in Table II and the Newman projection along the P-C(1) bond (Figure 1). Ste-

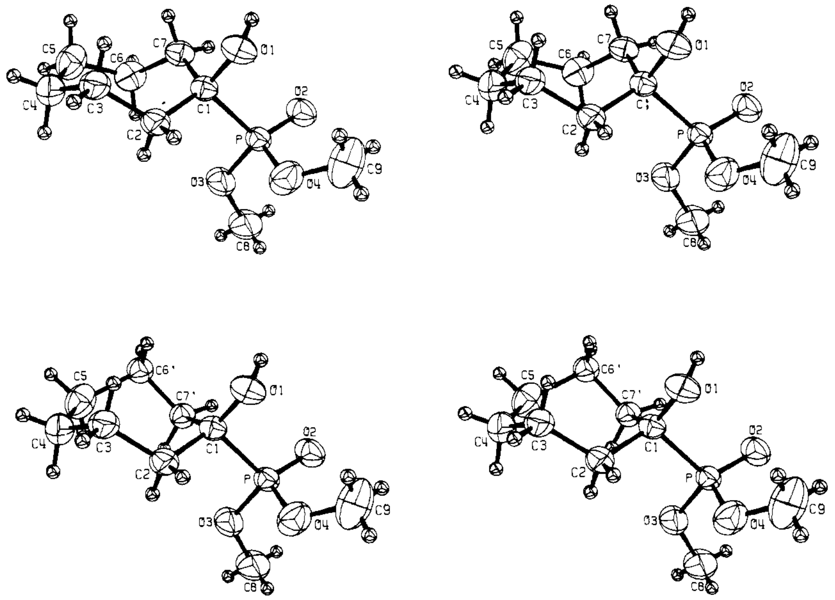

Figure 2. Stereoscopic views of the twist-chair (top) and the chair (bottom) conformers; the thermal ellipsoids correspond to 50% probability. In the chair conformer the hydrogen atoms attached to C(5), C(6'), and C(7') are shown in calculated positions.

**Table III.** Bond Lengths (in Ångströms) and Bond Angles (in Degrees)[a]

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.531 | C(7)-C(1)-C(2) | 114.8 |
| C(2)-C(3) | 1.527 | C(7')-C(1)-C(2) | 107 |
| C(3)-C(4) | 1.509 | C(1)-C(2)-C(3) | 115.5 |
| C(4)-C(5) | 1.507 | C(2)-C(3)-C(4) | 113.7 |
| C(5)-C(6) | 1.535 | C(3)-C(4)-C(5) | 116.1 |
| C(5)-C(6') | 1.60 | C(4)-C(5)-C(6) | 116.6 |
| C(6)-C(7) | 1.512 | C(4)-C(5)-C(6') | 119 |
| C(6')-C(7') | 1.52 | C(5)-C(6)-C(7) | 114.5 |
| C(7)-C(1) | 1.529 | C(5)-C(6')-C(7') | 104 |
| C(7')-C(1) | 1.72 | C(6)-C(7)-C(1) | 117.2 |
| C(1)-O(1) | 1.433 | C(6')-C(7')-C(1) | 116 |
| C(1)-P(1) | 1.829 | C(2)-C(1)-O(1) | 107.1 |
| P(1)-O(2) | 1.465 | C(7)-C(1)-O(1) | 109.3 |
| P(1)-O(3) | 1.568 | C(2)-C(1)-P(1) | 109.7 |
| P(1)-O(4) | 1.568 | C(7)-C(1)-P(1) | 111.7 |
| O(3)-C(8) | 1.441 | O(1)-C(1)-P(1) | 103.6 |
| O(4)-C(9) | 1.431 | C(1)-P(1)-O(2) | 114.5 |
| | | C(1)-P(1)-O(3) | 103.7 |
| | | C(1)-P(1)-O(4) | 107.0 |
| | | O(2)-P(1)-O(3) | 114.9 |
| | | O(2)-P(1)-O(4) | 113.0 |
| | | O(3)-P(1)-O(4) | 102.7 |
| | | P(1)-O(3)-C(8) | 121.3 |
| | | P(1)-O(4)-C(9) | 121.8 |

[a] Estimated standard deviations are 0.002-0.004 Å and 0.1-0.2°, 10 times larger for values involving C(6') and C(7').

reoscopic views of both conformers are shown in Figure 2. It is clear that the major conformer corresponds to the most stable twist-chair conformation while the minor conformer represents the somewhat less stable chair. In both cases the two substituents are in expected orientations. Hendrickson predicted[12] that the preferred conformation for a geminate-disubstituted cycloheptane would be a twist-chair with both substituents in isoclinal positions, i.e., attached to the carbon atom through which the twofold axis passes. In the chair conformation the bulkier dimethylphosphonate group is at the equatorial site.

Table III presents bond lengths and bond angles in both conformers. Instead of being equal, the bond lengths within the cycloheptane ring fall into two distinct categories: four of them are in the range 1.527-1.535 Å, i.e., within two standard deviations of the expected value (1.532 Å), while three others range from 1.507 to 1.512 Å, deviating from the expected length by $7\sigma$. We cannot offer a convincing explanation of these results. It is difficult to see how the observed disorder could be implicated. Firstly, each of the disordered carbon atoms was refined satisfactorily in both alternative positions and, secondly, two of the abnormal bonds, C(3)-C(4) and C(4)-C(5), involve atoms which are not disordered. Furthermore, these two bonds are too far removed from the two ring substituents for the latter to be responsible for this bond contraction. It should also be noted (Table IV) that none of the ring atoms exhibit excessively large or anisotropic thermal motion. Nevertheless, thermal motion may be responsible for these anomalous bond lengths. The range of C-H bond lengths is 0.87-1.02 Å, while the O-H bond is 0.86 Å long; the estimated standard deviations for these bonds are 0.02-0.04 Å. These values are in good agreement with results of other x-ray analyses and, as usual, they are shorter than the actual bond lengths. The C-C-H and H-C-H angles in the cycloheptane ring range from 102 to 113°. In view of the esds (2-3°) it is not possible to present a statistically meaningful assessment of these angles.

The geometry of the dimethylphosphonate group agrees very well with previously published values.[13,14] Using a formula proposed by Cruickshank,[15] we can calculate $\pi$-bond orders for the two types of P-O bonds in this group. The results indicate a $\pi$-bond order of 0.74 for the shorter bond and 0.43 for the two longer bonds, the total amount of $\pi$ bonds thus being 1.60. These values can be compared with those recently calculated[16] on the basis of P-O stretching force constants in methylphosphonic acid: 0.68 for the shorter bond and 0.47 for the two longer bonds for a total $\pi$-bond order of 1.62.

In the crystal, pairs of molecules are joined by two equivalent intermolecular hydrogen bonds. These are formed by a donation of the hydroxyl proton to the unmethylated oxygen of the phosphonate group in a molecule situated across a center of symmetry. An illustration is provided in the packing diagram (Figure 3). The geometry of this hydrogen bond is as follows: O(1)—H 0.86 (2), O(1)···O(2) 2.733 (2), H···O(2) 1.88 (3) Å; O(1)—H···O(2) 172 (2), O(1)···O(2)···H 2.6 (8) °. Apart from these there are no intermolecular contacts shorter than the sum of van der Waals radii.

The minor disorder encountered in this crystal structure may

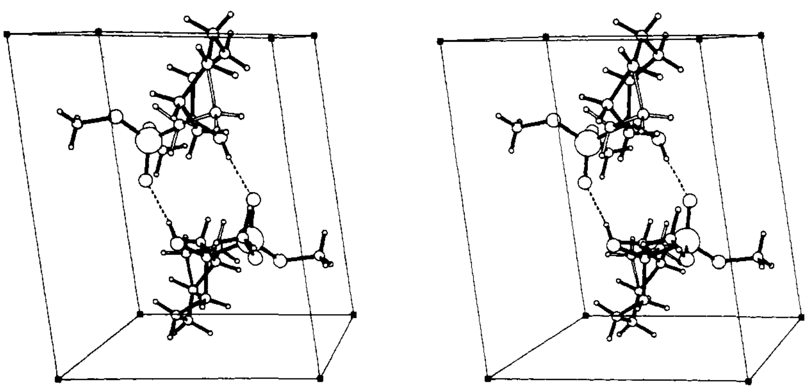

**Figure 3.** Stereoscopic view along $z$ of the contents of a unit cell. The directions of the axes are $x$, →; $y$, ↑; and $z$, ⊙. Bonds involving C(6′) and C(7′) are not filled in. Hydrogen bonds are indicated by dashed lines.

**Table IV.** Root-Mean-Square Amplitudes of Displacement (in Ångströms) Along the Principal Axes of Thermal Motion

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(1) | 0.178 | 0.192 | 0.203 | C(8) | 0.191 | 0.264 | 0.328 |
| C(2) | 0.176 | 0.202 | 0.229 | C(9) | 0.211 | 0.277 | 0.365 |
| C(3) | 0.192 | 0.199 | 0.240 | P(1) | 0.175 | 0.186 | 0.209 |
| C(4) | 0.204 | 0.226 | 0.279 | O(1) | 0.192 | 0.206 | 0.257 |
| C(5) | 0.194 | 0.249 | 0.300 | O(2) | 0.190 | 0.225 | 0.271 |
| C(6) | 0.193 | 0.237 | 0.264 | O(3) | 0.192 | 0.219 | 0.292 |
| C(7) | 0.183 | 0.211 | 0.230 | O(4) | 0.203 | 0.239 | 0.295 |

**Table V.** Bond Angles and Torsion Angles (in Degrees) in Twist-Chair and Chair Conformers of Cycloheptane[a]

| Conformer | $\theta_1$ | $\theta_2$ | $\theta_3$ | $\theta_4$ | $\omega_1$ | $\omega_2$ | $\omega_3$ | $\omega_4$ | rmsd[b] | Ref |
|---|---|---|---|---|---|---|---|---|---|---|
| Twist-chair | 115.0 | 113.0 | 115.0 | 116.0 | 39.1 | 88.1 | 72.3 | 54.3 | 2.1 | 17 |
| | 116.4 | 116.4 | 115.9 | 117.2 | 38.1 | 85.0 | 69.4 | 51.7 | 1.1 | 19 |
| | 116.5 | 116.5 | 117.3 | 119.1 | 36.3 | 80.8 | 70.3 | 56.2 | 3.4 | 20 |
| | 113.5 | 113.5 | 114.0 | 115.1 | 39.7 | 90.8 | 75.4 | 56.9 | 3.6 | 21 |
| | 114.8 | 116.3 | 114.1 | 116.3 | 38.8 | 86.5 | 69.2 | 50.8 | | *c* |
| Chair | 115.0 | 114.0 | 115.0 | 118.0 | 63.8 | 83.5 | 66.1 | 0 | 4.1 | 17 |
| | 115.7 | 115.2 | 115.1 | 118.5 | 62.6 | 81.9 | 64.7 | 0 | 4.9 | 19 |
| | 116.2 | 115.4 | 115.6 | 119.6 | 62.4 | 79.8 | 63.0 | 0 | 5.8 | 20 |
| | 112.5 | 112.7 | 113.1 | 116.6 | 67.1 | 88.1 | 68.8 | 0 | 2.3 | 21 |
| | 107 | 115.6 | 112.7 | 116.4 | 67 | 89.2 | 70.1 | 1 | | *c* |

[a] In both conformers $\theta_2 = \theta_7$, $\theta_3 = \theta_6$, $\theta_4 = \theta_5$; in the twist-chair $\omega_1 = \omega_7$, $\omega_2 = \omega_6$, $\omega_3 = \omega_5$, while in the chair $\omega_1 = -\omega_7$, $\omega_2 = -\omega_6$, $\omega_3 = -\omega_5$. [b] Root-mean-square deviations of calculated values from our experimental values. [c] This work; weighted averages of ideally equivalent absolute values.

be considered serendipitous since it provides us with information about both main forms of the chair/twist-chair pseudorotation family. We are therefore for the first time in a position to make valid comparisons between experimental data and results obtained from different theoretical calculations. Flapper and Romers[7] listed bond angles and torsion angles which they calculated on the basis of force fields suggested by Hendrickson,[17] Allinger[18] (modified by Altona[19]), Lifson,[20] and Boyd.[21] In Table V we compare those angles with the ones we found in our structure. For the twist-chair the best agreement is with Allinger's values followed by Hendrickson's values. A root-mean-square deviation of 1.1° for eight angles is remarkably low. In the case of the chair conformer the agreement is clearly best with the angles calculated with Boyd's field. Boyd's model of a cycloheptane chair is distinctly more puckered than the other three, as indicated by smaller bond angles and larger torsion angles. The chair we found is slightly more puckered than Boyd's.

One of the questions of interest concerns the relative energy of the chair form with respect to the most stable twist-chair. Since the crystal lattice was capable of accommodating both conformers simultaneously, the relative abundance of the two forms must be significant. From the refined values of occupancy factors (0.93 and 0.07) we can derive a value of 1.5 (1) kcal/mol for $\Delta E$. This value can be considered as the sum of two energy differences: (a) the difference between the chair and the twist-chair forms of cycloheptane and (b) the difference attributable to the substituents. Some idea about the latter effect can be obtained from Hendrickson's calculations of strain energies of methylcycloheptanes.[12] His results indicated that in a twist-chair conformation an excess energy of 0.5 kcal/mol can be associated with a methyl substituent in the isoclinal position, while in the chair form the excess amounts to 0.4 and 1.6 kcal/mol for methyl groups in the equatorial and axial positions, respectively, of C(1). Thus, a pseudorotation of 1,1-dimethylcycloheptane from a twist-chair to a chair increases the energy by 2.0 kcal/mol, of which 1.0 kcal/mol represents the conformational difference,[5,19] and 1.0 kcal/mol is attributable to moving a methyl group from an isoclinal to an axial orientation. The other methyl group can be ignored because it moves from an isoclinal to an equatorial site, both of which are essentially free of strain. By subtracting the conformational energy difference from the total difference derived from this crystal structure analysis, we obtain a value of 0.5 (1) kcal/mol which is due to moving a hydroxyl group from an isoclinal to an axial position at C(1). This appears reasonable when one considers that a hydroxyl group is much smaller than a methyl group. Furthermore, this value is comparable with the energy increase associated with moving a hydroxyl group from an equatorial to an axial orientation in a cyclohexane ring. On the basis of IR data Masschelein[22] calculated 0.38 kcal/mol, while Neelakantan[23] obtained 0.65 kcal/mol from Raman spectroscopy.

$^{13}$C NMR affords a method of examining the conformation of **1** in solution. The vicinal $^{13}$C-C-C-$^{31}$P coupling, to C(3) and C(6) from P, was found to be 10.9 Hz. Employing model compounds[3,4] and the torsion angles we observed in the twist-chair, the expected coupling is $\sim$6.5 Hz, if 12.6 Hz is used for $\omega \simeq 170°$ and 0.5 Hz for $\omega = 90°$. The observed coupling of 10.9 Hz suggests that in solution there is an enhanced population of chair relative to twist-chair compared with the solid phase. Using 12.5-13.0 Hz as a value for $\omega \simeq 170°$, it can be calculated that $\sim$65% of the solution conformation of **1** is in the chair form. It is difficult to rationalize the apparent preference for the chair form in solution. It should be noted, however, that the energy difference between chair and twist-chair is small and subtle features of solvation may bias the conformational equilibrium.

**Acknowledgment.** G.W.B. acknowledges financial support of this work from the National Research Council of Canada.

**Supplementary Material Available:** Listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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# Electrochemical and Electron Paramagnetic Resonance Studies of a Series of 1,4-Diphosphoniacyclohexa-2,5-diene Salts. Electrochemical Generation of the Radical Cations of a Series of Diphosphabenzene Compounds

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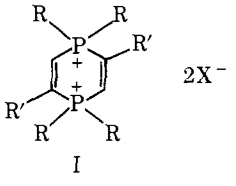
*Received March 30, 1977*

**Abstract:** Electrochemical studies were conducted on a series of 1,4-diphosphoniacyclohexa-2,5-diene salts (1), and these salts were found to give stable one-electron-reduction products. These stable radical cations were studied by electron paramagnetic resonance. Evidence for significant conjugative interaction by the tetravalent phosphorus atoms in these radical cations is presented.

Most phosphonium salts are known to cleave upon reduction.[2-7] We recently reported that certain 1,4-diphosphoniacyclohexa-2,5-diene salts (I) could be reduced at low potentials (−0.4 to −1.0 V) in a one-electron step to stable radical cations.[8,9] This unique behavior of compounds of structure I suggests stabilization of the radical cation by conjugative interaction from the phosphonium moiety since the reduction products of neither ethylene nor $R_4P^+$ are stable. The concept of d$\pi$-p$\pi$ bonding involving phosphorus has been a subject of controversy for a number of years.[10,11] From the electrochemistry of I and related compounds and the electron paramagnetic resonance (EPR) of the radical cations from reduction of I, the significance of conjugative interaction in $I^{+\cdot}$ is evaluated in this paper.



I

Previous electrochemical reduction of compounds I led to saturation of the double bonds.[15]

## Results

Electrochemical data for the first reduction wave (Figure 1) of compounds II-XVI are presented in Table I. The stability of the reduction products is indicated by the values of $i_{pa}/i_{pc}$ being near unity. The reversibility of the electron transfer is indicated by $E_{3/4} - E_{1/4}$ and $E_{pa} - E_{pc}$ being near the one-