

The enthalpies of transfer of the divalent cations and the alkali metal ions from water to the protic solvents methanol and formamide are exothermic. The endothermic transfer of all cations to methanol and formamide from DMF and DMSO is attributable to ion-solvent interactions which disrupt the hydrogen-bonded solvent-solvent interactions that occur in both  $\text{CH}_3\text{OH}$  and  $\text{HCONH}_2$ . In the case of methanol the endothermicity is enhanced by the greater donor power of DMF and DMSO, relative to methanol. Transfer of cations from formamide to dimethylformamide is a strongly exothermic transfer. These solvents use a similar  $\text{NC}=\text{O}$  grouping for cation solvation and are of comparable donor strength so that cation-solvent interactions are likely to be comparable. The exothermicity of transfer is a function of the hydrogen-bonded solvent-solvent interactions in formamide which are absent in DMF and which re-form when cations are transferred from formamide to DMF.

The enthalpies of transfer of many small anions, which are strong hydrogen bond acceptors, from water to dipolar aprotic solvent are endothermic. This is be-

cause strong anion-water hydrogen-bonding interactions are lost and this outweighs the gain of water-water H bonds (*vide supra*) when these anions are transferred from water to dipolar aprotic solvents. However, the enthalpies of transfer of  $\text{ClO}_4^-$  from water to all of the nonaqueous solvents are strongly exothermic. The perchlorate ion is a very weak H-bond acceptor.<sup>2</sup>

Transfer from water of the  $\text{ClO}_3^-$  anion, which has a pyramidal structure, is less exothermic than transfer of  $\text{ClO}_4^-$ . This is consistent with a loss of stronger  $\text{ClO}_3^-$ -water interactions due to the greater hydrogen-bonding acceptor ability of  $\text{ClO}_3^-$  and its lower polarizability, relative to  $\text{ClO}_4^-$ . The small, usually endothermic enthalpies of transfer of the  $\text{CF}_3\text{SO}_3^-$  ion from water indicate that this anion is a stronger hydrogen-bond acceptor than  $\text{ClO}_4^-$ , a much weaker acceptor than  $\text{Cl}^-$ , and a slightly weaker acceptor than  $\text{ClO}_3^-$ .

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## The Crystal and Molecular Structure of $\alpha$ -Acetoxy- $\alpha$ ,2-*anti*-diphenylmethylenecyclohexane

F. P. van Remoortere\* and J. J. Flynn

Contribution from the Dow Chemical Company, Midland, Michigan 48640.

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**Abstract:** The crystal and molecular structure of  $\alpha$ -acetoxy- $\alpha$ ,2-*anti*-diphenylmethylenecyclohexane,  $\text{C}_{21}\text{H}_{26}\text{O}_2$ , has been determined by a single-crystal, three-dimensional, X-ray diffraction study. The compound crystallizes in space group  $Pbca$  with lattice parameters  $a = 24.157 \pm 0.006$ ,  $b = 16.758 \pm 0.004$ , and  $c = 8.535 \pm 0.002$  Å ( $Z = 8$ ). The intensities of 2929 independent reflections were measured on a Picker automatic diffractometer (Cu K $\alpha$  radiation) and the structure was solved by the symbolic addition method. Full-matrix least-squares refinement of atom positions, hydrogen isotropic temperature factors, and anisotropic thermal parameters for carbons and oxygens converged at a final  $R_1 = 6.5\%$  for the 1722 reflections above background. The cyclohexylidene system is found in a flattened chair conformation with the 2-phenyl substituent axial as required by the theory of  $A^{(1,3)}$  strain. Torsion angles in the ring range from  $52.9$  to  $57.1^\circ$  (average  $55.3^\circ$ ), and internal bond angles at  $\text{sp}^3$  hybridized carbons average to  $110.7^\circ$ . Except for the  $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$  bond distances of  $1.503$  and  $1.515$  Å and the  $\text{C}(2)\text{-C}(1)\text{-C}(6)$  angle of  $114.0^\circ$ , metric parameters in the saturated ring conform quite closely to values observed in cyclohexanes. The  $\text{C}(\text{sp}^2)\text{-O}$  bond lengths in the acetoxy group are  $1.427$  and  $1.358$  Å for the bonds to the methylene and carbonyl carbon atoms, respectively. Bond distances and angles in the aromatic rings are in good agreement with literature values.

It has long been recognized that of the two possible conformers of a cyclohexane ring the chair is far more stable than the boat<sup>1-3</sup> and that substituents, in all but a few cases, tend to occupy equatorial positions.<sup>3</sup> However, the basic structural parameters of the cyclohexane system, which define essentially a flattened chair conformation, have been measured only during the last decade. For cyclohexane itself, electron diffraction analysis has given a value of  $111.9^\circ$  for the internal bond angle,<sup>4</sup> and X-ray studies of several of its sub-

stituted derivatives<sup>5-7</sup> have determined mean ring angles ranging from  $110.6$  to  $112.1^\circ$ . As a result of minimization of bond angle strain, the internal angle thus appears to lie between the tetrahedral angle and the  $n$ -paraffin angle of  $112.7^\circ$ .<sup>8</sup> In addition, torsional strain is minimized by reducing the torsion angle from an ideal  $60^\circ$  to values ranging from  $52.9$  to  $57.1^\circ$ .<sup>5-7</sup>

While there is ample experimental evidence indicating that the chair form is also the predominant ground-state conformation of six-membered rings containing one  $\text{sp}^2$

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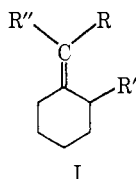
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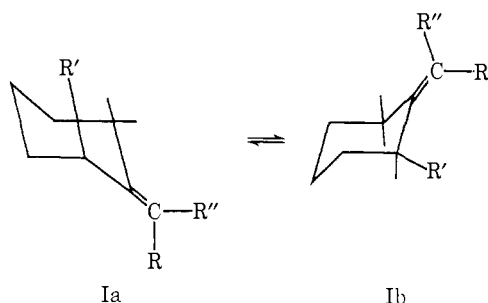
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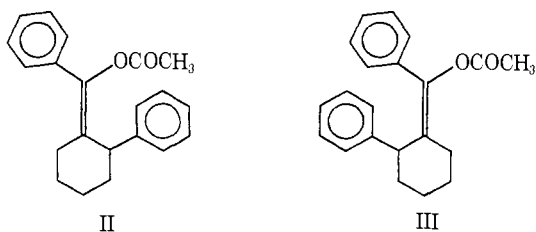
hybridized carbon atom (such as cyclohexanone<sup>9</sup> and methylenecyclohexane<sup>10</sup>) definitive structural parameters for these molecules are still lacking,<sup>11</sup> and even the stereochemistry of substituted methylenecyclohexanes has not been thoroughly investigated by modern structural methods. The situation pertaining to methylenecyclohexanes substituted at, and allylically to, the double bond was discussed in 1965 when Johnson and Malhotra introduced the concept of A<sup>(1,3)</sup> strain.<sup>12</sup> Their proposal states that if R and R' are moderate in size in systems such as I they will interfere and the con-



formational equilibrium should favor that form having the axial substituent (Ia). If the groups R and R' are small and do not interfere with one another, then conformation Ib should be formed.



The stereochemical theorem of A<sup>(1,3)</sup> strain, which was formulated as a result of experience with the stereochemical behavior of molecules containing substituted allylic groups associated with six-membered rings, was based on energy considerations assuming a near-planar arrangement of the grouping R'CC=CRR''. However, Malhotra and Johnson's interpretation<sup>13</sup> of the nmr spectra which supported the assignment predicted by this theorem for II and III was challenged by



Zimmerman and Mariano.<sup>14</sup> More recently Bordwell and Yee<sup>15</sup> have concluded that 2-phenylcyclohexane-nitronate ions exist in the conformation where the 2

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substituent assumes an equatorial rather than an axial position.

The present single-crystal X-ray diffraction investigation of  $\alpha$ -acetoxy- $\alpha$ ,2-*anti*-diphenylmethylenecyclohexane (II) was undertaken to determine whether the ground-state conformation in the solid is as predicted by the theory of A<sup>(1,3)</sup> strain. This system also affords a unique opportunity to compare directly the geometry of a six-membered ring containing one sp<sup>2</sup> hybridized carbon atom with the familiar cyclohexane conformation.

## Experimental Section

A sample of  $\alpha$ -acetoxy- $\alpha$ ,2-*anti*-diphenylmethylenecyclohexane, recrystallized from petroleum ether (bp 30–60°), was supplied by F. Johnson. The colorless crystals (mp 54–55°) have a tabular habit with well-defined faces. A crystal of dimensions 0.12 × 0.20 × 0.33 mm (along *a*, *b*, and *c*, respectively) was selected and mounted in a thin-walled Lindemann glass capillary with the *c* axis of the crystal approximately parallel to the capillary axis. The crystal was then aligned and examined by photographic methods on a Weissenberg goniometer to determine the space group and preliminary lattice constants. The reciprocal lattice symmetry *D*<sub>2h</sub> and the reflection conditions *hk*0 (*h* = 2*n*), *h*0*l* (*l* = 2*n*), and 0*kl* (*k* = 2*n*) recorded on the *hk*0 and *hk*1 Weissenberg levels establish the space group uniquely as *Pbca* (No. 61, *D*<sub>2h</sub><sup>15</sup>). The crystal was then carefully centered on a Picker four-circle goniostat, and the dimensions of the orthorhombic cell were calculated by least-squares refinement of the setting angles of 19 reflections with Cu K $\alpha$  radiation ( $\lambda$  1.5418 Å). The lattice parameters *a* = 24.157 ± 0.006, *b* = 16.758 ± 0.004, and *c* = 8.535 ± 0.002 Å (at 25°) are consistent with a calculated density of 1.178 g cm<sup>-3</sup> for molecular weight 306.41 and *Z* = 8. The estimated standard deviations of the lattice constants, as computed in the least-squares analysis, were a factor of 10 better than the errors assigned above, which reflect our experience with systematic errors and reproducibility of results under different experimental conditions.

Intensity data were gathered using the  $\theta$ -2 $\theta$  scan mode of the diffractometer with Ni filtered Cu K $\alpha$  radiation. The take-off angle of the tube was 3°, and a counter aperture 6.0 × 6.0 mm was placed 30 cm from the crystal; 1.5-mm diameter incident- and exit-beam collimators were used to restrict stray radiation. The scan speed was 2°/min over 2 $\theta$  angles of 2° +  $\Delta$ , where  $\Delta$  is the separation of the K $\alpha$  doublet; this range was sufficient to allow for the observed mosaic spread of the crystal. Two stationary crystal stationary counter background counts of 15 sec were taken at each end of the scan. The reciprocal lattice was recorded to near the instrumental limit ( $\sin \theta = 0.906$ ) and a total of 2929 independent reflections were measured. A test reflection (5, 3, 1) monitored after every 50 measurements showed good stability. An error  $\sigma(I) = [(0.02I)^2 + N_0 + k^2N_b]^{1/2}$  was assigned to the net intensity  $I = N_0 - kN_b$  of each reflection in order to establish the weights  $w(F) = 4F^2/\sigma^2(F^2)$  for subsequent least-squares refinement, where the quantity  $\sum w(|F_0| - |F_c|)^2$  was minimized. Here *N*<sub>0</sub> is the gross count, *N*<sub>b</sub> is the background count, *k* is the ratio of scan time to background time, and the *F*<sup>2</sup> are the intensities corrected for Lorentz and polarization effects. The 1207 reflections for which *I* < 0 or *I*/ $\sigma(I)$  < 2.0 were denoted absent and omitted from the refinement. The linear absorption coefficient for Cu K $\alpha$  is 5.91 cm<sup>-1</sup>. Transmission factors were estimated to range from about 0.82 to 0.93, but no corrections were made.

**Solution and Refinement of the Structure.** A scale factor (2.0) and overall temperature factor (*B*<sub>0</sub> = 4.2 Å<sup>2</sup>) were computed by Wilson's method and used to calculate a set of normalized structure factors (*E*'s). Assuming symbols for seven reflections, the phases of 403 of the largest *E*'s were determined by the symbolic addition method using the program MAGIC of Dewar and Stone,<sup>16</sup> which implements the Karle-Hauptman  $\sigma$ -2 relationship<sup>17</sup>

$$s(E_h) = s\left(\sum_k E_k E_{h-k}\right)$$

(16) The Fortran package MAGIC by R. B. K. Dewar and A. Stone, The University of Chicago, Chicago, Ill., consists of the programs MAGIC, LINK, and SYMPL which allow the application of the symbolic addition procedure to centrosymmetric crystals.

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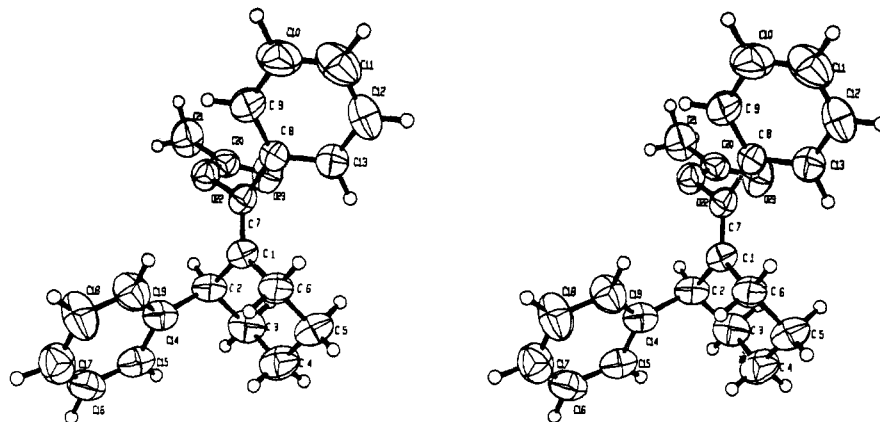


Figure 1. Stereoscopic view of  $\alpha$ -acetoxy- $\alpha,2$ -anti-diphenylmethylenecyclohexane showing the ellipsoids of thermal motion and the numbering system.

where  $s$  means "sign of" and  $h$  and  $k$  are the index triples of the reflections. In order to determine the most probable sign combination, the program LINK then examined the symbol equivalences generated by MAGIC and calculated the inconsistency index

$$I = \sum_j N_j / (1.000001 - P_j)$$

for each sign combination, where  $N_j$  and  $P_j$  are respectively the MAGIC iteration number and the probability for symbol equivalence  $j$ . The most probable solution ( $I = 2165$ ) was only moderately favored over three other sign combinations ( $I$  from 7237 to 9863). Reflections whose determination led to an inconsistency were rejected in SYMPL, and the 318 remaining  $E$ 's were given signs in accordance with the most probable combination, which assumed positive signs for (2, 3, 2), (18, 4, 3), (2, 15, 1), (11, 8, 5), (13, 7, 4), and (17, 5, 3) and a negative sign for (15, 10, 4). An  $E$  map<sup>18</sup> calculated from this solution showed a large number of peaks, of which six (with amplitudes ranging from 252 to 467 on an arbitrary scale) were tentatively identified as forming a phenyl group. On the basis of past experiences, a peak of intensity 1333, twice as strong as any other site, was believed to be the ether oxygen. Since similar inconsistency indices were found for three other sign combinations, maps based on these solutions were calculated<sup>18</sup> but no meaningful structure could be extracted. Starting from a different and enlarged set of eight reflections MAGIC was run again and identified the same sign combination as the most probable solution. At this stage a normal-sharpened three-dimensional Patterson function was calculated<sup>18</sup> against which the interactions resulting from the ether oxygen and the phenyl ring described above were systematically and successfully verified. With considerable difficulty the remaining atoms of the molecule were finally identified in the original  $E$  map. Their relative intensities ranged from 154 to 618. Eleven other peaks with amplitudes between 201 and 362 proved to be spurious. Subsequent least-squares refinement showed 27 (8.5%) phases determined in SYMPL to be incorrect. *A posteriori* application of the tangent formula<sup>19,20</sup> significantly improved this phase set, however, and converged after four cycles to a 97.7% correct solution.

Six cycles of least-squares refinement of the atomic positions and isotropic temperature factors of the 23 atoms found in the  $E$ -map, using a small computer, blocks of 72 variables and a set of 736 reflections, were not initiated.<sup>21,22</sup> On the basis of its bond distance and its temperature factor, the carbonyl oxygen was distinguished

from the methyl carbon after the first cycle and subsequently assigned an oxygen scattering factor. This refinement reduced

$$R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$$

from 0.294 to 0.132 and

$$R_2 = \{(\sum w[F_o - F_c]^2) / \sum wF_o^2\}^{1/2}$$

from 0.360 to 0.148. A difference map<sup>18</sup> revealed clearly the cyclohexylidene and phenyl hydrogens at their calculated positions with relative peak heights ranging from 86 to 190. The methyl hydrogens could also be identified in reasonable positions with amplitudes between 117 and 162. Refinement was continued<sup>22,23</sup> on a larger computer using full matrix least squares and including all 172? reflections above background. Anisotropic thermal motion was assumed for the heavier atoms and isotropic temperature factors were used for the hydrogens. After two cycles, in which  $R_1$  was reduced from 0.151 to 0.080 and  $R_2$  from 0.154 to 0.067, a correction for secondary extinction was applied to 11 strong low-order reflections that were systematically less intense than their calculated values.<sup>24</sup> Additional refinement<sup>23</sup> on all parameters converged in three more cycles to the final discrepancy indices of  $R_1 = 0.065$  and  $R_2 = 0.049$  for the 1722 reflections. In the final cycle the average shift in position parameters was  $0.02\sigma$  with a maximum shift of  $0.17\sigma$  for the heavier atoms and  $0.06\sigma$  with a maximum shift of  $0.48\sigma$  for the hydrogens. A final difference Fourier<sup>18</sup> showed no positive or negative density of magnitude in excess of  $0.22 \text{ e} \text{ \AA}^{-3}$ .

Atomic parameters and their estimated standard deviations are given in Table I, while bond distances and angles, together with standard deviations computed<sup>25</sup> from the variance-covariance matrix obtained in the final least-squares cycle, are listed in Table II. The root-mean-square components of thermal displacement along the principal axes, as defined by the anisotropic thermal parameters, are compiled in Table III. The directions of thermal motion may be inferred from Figure 1, in which the three-dimensional structure of the molecule is shown using ellipsoids to represent the anisotropic thermal motion.<sup>26</sup> A table of observed and calculated structure factors is available to the interested reader.<sup>27</sup>

## Discussion

Our results establish that the cyclohexylidene system adopts a chair conformation whereby the 2-phenyl substituent assumes an axial position as predicted by

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Table I. Final Structure Parameters<sup>a</sup> and Standard Deviations<sup>b</sup>

Atom	x	y	z	10 <sup>4</sup> β <sub>11</sub>	10 <sup>4</sup> β <sub>22</sub>	10 <sup>4</sup> β <sub>33</sub>	10 <sup>4</sup> β <sub>12</sub>	10 <sup>4</sup> β <sub>13</sub>	10 <sup>4</sup> β <sub>23</sub>
C(1)	0.1455 (1)	-0.0282 (2)	0.2562 (4)	16 (1)	31 (1)	161 (6)	-1 (1)	4 (2)	8 (3)
C(2)	0.1738 (1)	-0.0383 (2)	0.0991 (4)	19 (1)	34 (2)	183 (7)	-1 (1)	19 (2)	4 (3)
C(3)	0.2339 (1)	-0.0631 (2)	0.1286 (5)	19 (1)	50 (2)	245 (10)	-4 (1)	18 (2)	-3 (4)
C(4)	0.2385 (1)	-0.1365 (2)	0.2306 (6)	17 (1)	63 (3)	298 (12)	6 (1)	7 (3)	-2 (5)
C(5)	0.2087 (2)	-0.1254 (2)	0.3860 (5)	24 (1)	41 (2)	265 (11)	4 (1)	1 (3)	19 (4)
C(6)	0.1483 (1)	-0.1008 (2)	0.3592 (4)	19 (1)	38 (2)	174 (8)	-0 (1)	8 (2)	-1 (3)
C(7)	0.1201 (1)	0.0388 (2)	0.2973 (3)	16 (1)	35 (2)	149 (7)	-1 (1)	-5 (2)	7 (3)
C(8)	0.0924 (1)	0.0603 (2)	0.4449 (3)	14 (1)	36 (2)	145 (7)	-2 (1)	1 (2)	-4 (3)
C(9)	0.0415 (1)	0.0979 (2)	0.4415 (5)	18 (1)	70 (2)	212 (10)	8 (1)	-1 (3)	14 (4)
C(10)	0.0150 (2)	0.1197 (3)	0.5789 (6)	22 (1)	82 (3)	293 (13)	7 (1)	14 (3)	-41 (5)
C(11)	0.0391 (2)	0.1052 (3)	0.7189 (5)	29 (1)	85 (3)	218 (12)	-8 (2)	32 (4)	-32 (5)
C(12)	0.0895 (2)	0.0678 (2)	0.7260 (4)	31 (1)	67 (2)	141 (8)	-9 (1)	3 (3)	-4 (4)
C(13)	0.1161 (1)	0.0462 (2)	0.5898 (4)	20 (1)	46 (2)	165 (8)	-1 (1)	1 (2)	3 (3)
C(14)	0.1415 (1)	-0.0949 (2)	-0.0084 (4)	21 (1)	39 (2)	158 (7)	1 (1)	17 (2)	10 (3)
C(15)	0.1660 (2)	-0.1364 (2)	-0.1323 (4)	24 (1)	42 (2)	201 (9)	5 (1)	16 (3)	12 (3)
C(16)	0.1339 (2)	-0.1826 (2)	-0.2327 (4)	40 (1)	42 (2)	165 (9)	10 (2)	9 (3)	-6 (4)
C(17)	0.0785 (2)	-0.1893 (2)	-0.2144 (5)	33 (1)	56 (2)	182 (10)	-3 (2)	-5 (3)	4 (4)
C(18)	0.0534 (2)	-0.1500 (3)	-0.0948 (5)	29 (1)	90 (3)	178 (9)	-12 (2)	5 (3)	-24 (4)
C(19)	0.0847 (2)	-0.1019 (2)	0.0043 (4)	24 (1)	66 (2)	174 (8)	-4 (1)	17 (3)	-20 (4)
C(20)	0.1520 (1)	0.1594 (2)	0.1858 (4)	24 (1)	35 (2)	145 (7)	2 (1)	3 (2)	2 (3)
C(21)	0.1394 (2)	0.2211 (2)	0.0645 (5)	42 (2)	42 (2)	218 (10)	-5 (2)	-17 (4)	25 (4)
O(22)	0.1143 (1)	0.0994 (1)	0.1809 (2)	20 (1)	36 (1)	153 (4)	-1 (1)	-7 (1)	8 (2)
O(23)	0.1899 (1)	0.1605 (1)	0.2736 (3)	27 (1)	54 (1)	253 (6)	-10 (1)	-21 (2)	23 (2)
				B, Å <sup>2</sup>					
H(2)	0.173 (1)	0.013 (2)	0.041 (3)	5.5 (0.9)					
H(31)	0.252 (1)	-0.014 (2)	0.185 (3)	7.3 (1.0)					
H(32)	0.255 (1)	-0.067 (2)	0.019 (3)	7.6 (1.0)					
H(41)	0.277 (1)	-0.144 (2)	0.255 (4)	8.0 (1.1)					
H(42)	0.222 (1)	-0.177 (2)	0.172 (4)	9.5 (1.6)					
H(51)	0.229 (1)	-0.073 (2)	0.447 (4)	9.9 (1.3)					
H(52)	0.208 (1)	-0.167 (1)	0.443 (3)	4.0 (0.9)					
H(61)	0.131 (1)	-0.143 (1)	0.303 (3)	4.7 (0.9)					
H(62)	0.129 (1)	-0.092 (1)	0.458 (3)	4.0 (0.8)					
H(9)	0.026 (1)	0.112 (2)	0.338 (4)	7.6 (1.2)					
H(10)	-0.021 (2)	0.155 (2)	0.565 (4)	12.6 (1.6)					
H(11)	0.022 (1)	0.121 (2)	0.815 (4)	6.7 (1.1)					
H(12)	0.107 (1)	0.058 (2)	0.825 (4)	7.8 (1.2)					
H(13)	0.153 (1)	0.018 (2)	0.589 (3)	6.2 (0.9)					
H(15)	0.206 (1)	-0.131 (1)	-0.137 (3)	3.7 (0.8)					
H(16)	0.152 (1)	-0.211 (2)	-0.315 (3)	7.3 (1.1)					
H(17)	0.054 (1)	-0.220 (2)	-0.287 (3)	7.4 (1.2)					
H(18)	0.010 (1)	-0.157 (2)	-0.084 (4)	10.1 (1.3)					
H(19)	0.068 (1)	-0.078 (1)	0.088 (3)	5.4 (1.0)					
H(211)	0.121 (2)	0.201 (2)	-0.012 (4)	10.4 (2.0)					
H(212)	0.101 (2)	0.247 (3)	0.097 (6)	17.4 (2.5)					
H(213)	0.165 (2)	0.260 (3)	0.054 (5)	14.2 (2.3)					

<sup>a</sup> The anisotropic thermal parameters are in the form  $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$ . <sup>b</sup> Standard errors are given in parentheses.

Malhotra and Johnson on the basis of A<sup>(1,3)</sup> strain.<sup>12</sup> The geometry of this six-membered ring, which contains one sp<sup>2</sup> hybridized carbon atom, closely resembles the conformations reported for cyclohexane and its substituted derivatives. Although slightly shorter than the average length of 1.537 Å tabulated<sup>28</sup> for saturated hydrocarbons, the mean C(sp<sup>3</sup>)-C(sp<sup>3</sup>) bond distance of 1.524 Å compares well with the value of 1.528 Å determined in cyclohexane by electron diffraction<sup>4</sup> and the averages of 1.526,<sup>5</sup> 1.511,<sup>6</sup> 1.520,<sup>7</sup> and 1.529<sup>29</sup> found in substituted cyclohexanes by X-ray methods. The endocyclic C(sp<sup>3</sup>)-C(sp<sup>3</sup>) single bonds average 1.509 Å, in good agreement with the literature mean values ranging from 1.506 to 1.510 Å.<sup>28</sup> Internal bond angles at the sp<sup>3</sup> hybridized carbon atoms in the six-membered ring take a mean value of 110.7°, larger than the ideal tetrahedral value but within the range (110.6 to 112.7°) observed for cyclohexanes.<sup>4-7</sup> The ring angle of 114.0

± 0.3° spanned by the sp<sup>2</sup> hybridized carbon atom is significantly smaller than the ideal trigonal value and the mean values of 117.8 and 117.4 found in cyclohexane-1,4-dioxime<sup>30</sup> and cyclohexane-1,4-dione,<sup>31</sup> respectively, but is not unexpected in view of the C-C-C angle of 115.3 ± 0.1° reported for isobutylene.<sup>32</sup> Table IV compiles the torsion angles in the cyclohexylidene system. Their average value of 55.3° is within the range (52.9 to 57.1°) reported for cyclohexane derivatives,<sup>5-7</sup> and their spread is not larger than in disubstituted cyclohexanes.<sup>7</sup> These bond and torsion angle data clearly define a flattened chair conformation basically identical with cyclohexane itself, except for the slightly larger internal angle at the sp<sup>2</sup> hybridized carbon atom. Although steric requirements seem comparable in 2-substituted methylene cyclohexanes and 2-substituted cyclohexanenitronate ions, our data do not substantiate

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Table II. Bond Distances and Bond Angles<sup>a</sup>

A. Bond Distances, Å				B.				
Bond	Length	Bond	Length	Vertex	Atom 1	Atom 2		
Bonds in saturated ring		C(15)–C(16)	1.391 (5)	C(6)	C(1)	C(5)	110.4 (0.3)	
C(1)–C(2)	1.515 (4)	C(16)–C(17)	1.353 (5)		C(1)	H(61)	107 (2)	
C(1)–C(6)	1.503 (4)	C(17)–C(18)	1.360 (5)		C(1)	H(62)	111 (1)	
C(2)–C(3)	1.531 (4)	C(18)–C(19)	1.392 (5)		C(5)	H(61)	107 (1)	
C(3)–C(4)	1.511 (5)				C(5)	H(62)	112 (1)	
C(4)–C(5)	1.521 (5)	Carbon–hydrogen bonds			H(61)	H(62)	110 (2)	
C(5)–C(6)	1.533 (5)	C(2)–H(2)	0.99 (3)	C(7)	C(1)	C(8)	130.1 (0.3)	
Carbon–oxygen bonds		C(3)–H(31)	1.05 (3)		C(1)	O(22)	117.6 (0.3)	
C(7)–O(22)	1.427 (3)	C(3)–H(32)	1.06 (3)		C(8)	O(22)	112.1 (0.2)	
C(20)–O(22)	1.358 (3)	C(4)–H(41)	0.95 (3)	C(8)	C(7)	C(9)	120.0 (0.3)	
C(20)–O(23)	1.182 (3)	C(4)–H(42)	0.93 (3)		C(7)	C(13)	122.4 (0.3)	
Exocyclic carbon–carbon bonds		C(5)–H(51)	1.13 (3)		C(9)	C(13)	117.6 (0.3)	
C(1)–C(7)	1.326 (4)	C(5)–H(52)	0.84 (2)	C(9)	C(8)	C(10)	121.0 (0.4)	
C(2)–C(14)	1.534 (4)	C(6)–H(61)	0.95 (2)		C(8)	H(9)	117 (2)	
C(7)–C(8)	1.471 (4)	C(6)–H(62)	0.97 (2)		C(8)	H(9)	121 (2)	
C(20)–C(21)	1.495 (5)	C(9)–H(9)	0.99 (3)	C(10)	C(10)	C(11)	120.1 (0.4)	
Bonds in phenyl rings		C(10)–H(10)	1.06 (4)		C(9)	H(10)	116 (2)	
C(8)–C(9)	1.382 (4)	C(11)–H(11)	0.96 (3)		C(11)	H(10)	124 (2)	
C(8)–C(13)	1.383 (4)	C(12)–H(12)	0.95 (3)	C(11)	C(10)	C(12)	120.3 (0.4)	
C(9)–C(10)	1.385 (5)	C(13)–H(13)	1.01 (3)		C(10)	H(11)	121 (2)	
C(10)–C(11)	1.352 (5)	C(15)–H(15)	0.97 (2)		C(12)	H(11)	118 (2)	
C(11)–C(12)	1.372 (5)	C(16)–H(16)	0.95 (3)	C(12)	C(11)	C(13)	119.8 (0.4)	
C(12)–C(13)	1.376 (4)	C(17)–H(17)	1.00 (3)		C(11)	H(12)	120 (2)	
C(14)–C(15)	1.397 (4)	C(18)–H(18)	1.07 (3)		C(11)	H(12)	120 (2)	
C(14)–C(19)	1.382 (4)	C(19)–H(19)	0.92 (2)	C(13)	C(8)	C(12)	121.2 (0.3)	
		C(21)–H(211)	0.86 (4)		C(8)	H(13)	116 (2)	
		C(21)–H(212)	1.06 (5)		C(12)	H(13)	123 (2)	
		C(21)–H(213)	0.90 (4)		C(12)	H(13)	123 (2)	
B. Bond Angles, deg								
Vertex	Atom 1	Atom 2						
C(1)	C(2)	C(6)	114.0 (0.3)					
	C(2)	C(7)	122.5 (0.3)	C(14)	C(2)	C(15)	123.1 (0.3)	
	C(6)	C(7)	123.5 (0.3)		C(2)	C(19)	120.7 (0.3)	
C(2)	C(3)	C(3)	108.3 (0.3)		C(15)	C(19)	116.0 (0.3)	
	C(1)	C(14)	111.7 (0.2)	C(15)	C(14)	C(16)	120.5 (0.3)	
	C(1)	H(2)	109 (1)		C(14)	H(15)	114 (2)	
	C(3)	C(14)	114.4 (0.3)		C(16)	H(15)	126 (2)	
	C(3)	H(2)	110 (2)	C(16)	C(15)	C(17)	121.8 (0.4)	
	C(14)	H(2)	103 (2)		C(15)	H(16)	119 (2)	
C(3)	C(4)	C(4)	112.6 (0.3)		C(17)	H(16)	119 (2)	
	C(2)	H(31)	105 (2)	C(17)	C(16)	C(18)	119.2 (0.4)	
	C(2)	H(32)	109 (2)		C(16)	H(17)	124 (2)	
	C(4)	H(31)	110 (2)		C(18)	H(17)	116 (2)	
	C(4)	H(32)	115 (2)	C(18)	C(17)	C(19)	119.6 (0.4)	
	H(31)	H(32)	104 (2)		C(17)	H(18)	117 (2)	
C(4)	C(3)	C(5)	111.7 (0.3)		C(19)	H(18)	123 (2)	
	C(3)	H(41)	107 (2)	C(19)	C(14)	C(18)	122.8 (0.4)	
	C(3)	H(42)	105 (2)		C(14)	H(19)	118 (2)	
	C(5)	H(41)	107 (2)		C(18)	H(19)	119 (2)	
	C(5)	H(42)	111 (2)	C(20)	C(21)	O(22)	110.8 (0.3)	
	H(41)	H(42)	115 (3)		C(21)	O(23)	125.9 (0.3)	
C(5)	C(4)	C(6)	110.6 (0.3)		O(22)	O(23)	123.3 (0.3)	
	C(4)	H(51)	107 (2)	C(21)	C(20)	H(211)	112 (3)	
	C(4)	H(52)	114 (2)		C(20)	H(212)	106 (3)	
	C(6)	H(51)	106 (2)		C(20)	H(213)	115 (3)	
	C(6)	H(52)	107 (2)		H(211)	H(212)	85 (3)	
	H(51)	H(52)	112 (2)		H(211)	H(213)	124 (4)	
					H(212)	H(213)	110 (4)	
					O(22)	C(7)	C(20)	116.1 (0.2)

<sup>a</sup> Standard errors calculated from the variance–covariance matrix obtained in the final least-squares cycle are given in parentheses.

a deformed chair conformation for the ground state of the latter ions.<sup>15</sup>

The observed orientation of the axial phenyl (A) appears to reflect an energy minimum with respect to rotation about the C(2)–C(14) single bond, and the inter-

action of its ortho hydrogen atoms with the axial 4- and 6-hydrogen atoms may well restrict its rotation in the isolated molecule. The phenyl is oriented so that the bisector of the C(1)–C(2)–C(3) angle lies approximately in the plane normal to the ring resulting in distances of



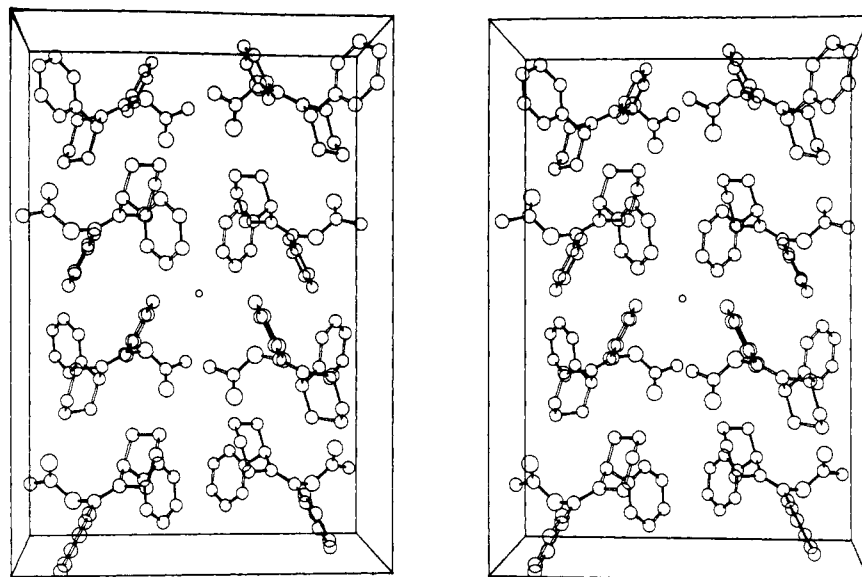


Figure 2. Three-dimensional view of molecular packing in  $\alpha$ -acetoxy- $\alpha$ ,2-*anti*-diphenylmethylenecyclohexane as viewed down the  $z$  axis. The  $x$  axis is vertical and the  $y$  axis is horizontal. The origin of the box is at  $0, -1/4, 0$ .

Table V. Least-Squares Planes<sup>a,b</sup>

Atom	Plane					
	1	2	3	4	5	6
1	C(1)	C(1)	C(1)	C(7)	C(8)	C(14)
2	C(2)	C(2)	C(7)	O(22)	C(9)	C(15)
3	C(6)	C(6)	C(8)	C(20)	C(10)	C(16)
4	C(7)	C(7)	O(22)	O(23)	C(11)	C(17)
5	C(8)			C(21)	C(12)	C(18)
6	O(22)				C(13)	C(19)
$m_1$	20.683	20.621	20.777	-13.448	10.938	3.214
$m_2$	6.196	5.663	6.695	8.534	14.930	-13.217
$m_3$	3.080	3.384	2.708	5.602	-0.292	5.123
$d$	3.612	3.704	3.537	0.357	1.784	1.657
$\Delta d_1$	0.012	0.003	-0.009	0.024	-0.002	0.009
$\Delta d_2$	0.052	-0.001	0.024	-0.033	0.002	0.001
$\Delta d_3$	-0.062	-0.001	-0.008	0.000	-0.002	-0.005
$\Delta d_4$	0.029	-0.001	-0.007	-0.008	0.004	-0.001
$\Delta d_5$	0.044			0.016	-0.004	0.011
$\Delta d_6$	-0.075				0.003	-0.015

<sup>a</sup> The planes are defined by the equation  $m_1x + m_2y + m_3z = d$ . <sup>b</sup>  $\Delta d_i$  refers to the deviation in Å of atom  $i$  from the least-squares plane.

C(sp<sup>2</sup>)-O bond of 1.358 Å is within the range of values observed for other C(sp<sup>2</sup>)-O bonds<sup>7</sup> and may involve resonance structure IV. However, although this resonance form includes a carbonyl single bond and thus would predict a long carbon-oxygen distance there, no unusual lengthening is observed. In fact a rather short value,  $1.182 \pm 0.003$  Å, is measured for the carbonyl bond length. (A correction for thermal motion assuming the oxygen atom rides on the carbon would increase this value to  $1.216 \pm 0.003$  Å.) This short distance is consistent with the shift of the carbonyl stretching frequency to  $1760\text{ cm}^{-1}$  for enol and phenol acetates, compared to the average of  $1735\text{ cm}^{-1}$  reported for esters.<sup>35</sup> Because structure IV cannot explain both anomalously short distances, further studies of the behavior of carbon-oxygen bond lengths in unsaturated systems appear to be desirable.

Phenyl B is planar within experimental error (Table V,

plane 5), while phenyl A shows small and possibly significant deviations from planarity (Table V, plane 6). The atoms which deviate most from the least-squares plane show also the largest out-of-plane thermal vibrations (Figure 1). The 12 ( $n$ ) C-C bond distances ( $d_i$ ) in these rings have an average value  $\bar{d} = 1.377$  Å with a standard deviation

$$\sigma = \left[ \sum_{i=1}^n (\bar{d} - d_i)^2 / (n - 1) \right]^{1/2}$$

of  $0.015$  Å, approximately three times larger than the errors of  $0.004$  to  $0.005$  calculated<sup>24</sup> from the variance-covariance matrix. The hydrogen positions are reasonably well behaved with bond distances ranging from  $0.84$  to  $1.13$  Å (average value  $0.97$  Å) and from  $0.92$  to  $1.07$  Å (average value  $0.99$  Å) for bonds to sp<sup>3</sup> and sp<sup>2</sup> carbons, respectively. Hydrogen isotropic temperature factors range between  $3.7$  and  $17.4$  Å<sup>2</sup>.

Thermal motion and anisotropy, relatively small for atoms comprising the unsaturated system built on the

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exocyclic double bond, generally increase toward the extremities of the molecule (Table III and Figure 1). The largest thermal amplitudes are approximately in plane for phenyl B, but C(18) and C(19) display their largest vibrational components perpendicular to the plane of phenyl A.

The molecular packing can be seen in a three-dimensional view down the  $z$  axis in Figure 2. No unusually short intermolecular contacts are present. The only intermolecular approaches smaller than 3.75 Å are C(3) ( $x, y, z$ )  $\cdots$  C(13) ( $1/2 - x, \bar{y}, -1/2 + z$ ) ( $3.649 \pm 0.005$  Å), C(6) ( $x, y, z$ )  $\cdots$  C(16) ( $x, -1/2 - y, 1/2 + z$ ) ( $3.729 \pm 0.005$  Å), and C(12) ( $x, y, z$ )  $\cdots$  C(19) ( $x, y, 1 + z$ ) ( $3.708 \pm 0.005$  Å) along the  $x, y,$  and  $z$  directions, respectively. Molecules related by centers of symmetry pack with their phenyl B rings parallel; the distance 3.86

Å between such planes is about 0.46 Å longer than the closest packing between phenyls.<sup>36</sup>

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**Supplementary Material Available.** A listing of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche 105  $\times$  148 mm, 24 $\times$  reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6593.

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## Reactions of Dimethyl Acetylenedicarboxylate and Related Acetylenes with Methylplatinum(II) Complexes

T. G. Appleton, M. H. Chisholm, H. C. Clark,\* and K. Yasufuku

Contribution from the Department of Chemistry, University of Western Ontario, London N6A 3K7, Ontario, Canada. Received January 18, 1974

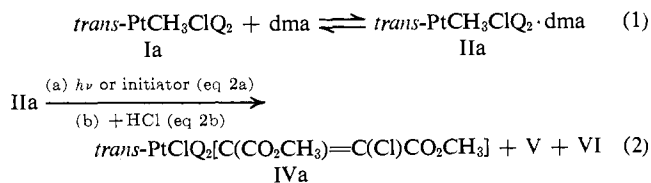
**Abstract:** The reaction of *trans*-PtXCH<sub>3</sub>Q<sub>2</sub> (X = Cl, Br, I; Q = P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) with RC $\equiv$ CCO<sub>2</sub>CH<sub>3</sub> affords *trans*-PtXQ<sub>2</sub>[C(COOCH<sub>3</sub>)=C(Cl)R] in the presence of a radical initiator (R = CO<sub>2</sub>CH<sub>3</sub>) or by addition of HCl (R = CO<sub>2</sub>CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, CH<sub>3</sub>, H). *trans*-PtXQ<sub>2</sub>[C(COOCH<sub>3</sub>)=C(COOCH<sub>3</sub>)CH<sub>3</sub>] is obtained from the reaction of *trans*-[PtCH<sub>3</sub>(acetone)Q<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> with the acetylene (R = CO<sub>2</sub>CH<sub>3</sub>) followed by treatment with LiX. Based on the formation of these products and other observations, a mechanism for the formation of the  $\beta$ -chlorovinylplatinum compound in CHCl<sub>3</sub> is proposed. This involves initial formation of the 1:1 complex with acetylene, followed by nucleophilic attack on the acetylene by HCl which is generated *via* a radical process.

Very recently, the possibility of a radical reaction of CH<sub>3</sub>O<sub>2</sub>CC $\equiv$ CCO<sub>2</sub>CH<sub>3</sub> (dma) with the methylplatinum bond of *trans*-PtCH<sub>3</sub>XQ<sub>2</sub> (Q = P(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), I (Ia has X = Cl), was reported.<sup>1</sup> Such an insertion reaction of an organometallic compound by a free radical process is very interesting and apparently consistent with other more recent reports<sup>2</sup> of radical behavior by organoplatinum complexes. We have now examined this and related reactions in detail.

The product previously identified<sup>1</sup> incorrectly as the insertion product, *trans*-PtXQ<sub>2</sub>[C(CO<sub>2</sub>CH<sub>3</sub>)=C(CO<sub>2</sub>CH<sub>3</sub>)CH<sub>3</sub>] (III) (IIIa has X = Cl), is now shown to be the  $\beta$ -chlorovinylplatinum compound, *trans*-PtXQ<sub>2</sub>-[C(CO<sub>2</sub>CH<sub>3</sub>)=C(Cl)CO<sub>2</sub>CH<sub>3</sub>] (IV) (IVa has X = Cl). The radical aspects of the reaction can be attributed to the radically induced formation of HCl which then participates in the formation of IV. We have also studied further the importance of the 1:1 adducts formed from some acetylenes and I.

## Results and Discussion

**Preparation and Identification of III and IV.** In chloroform solution, Ia and dma form the 1:1 adduct IIa which undergoes further reaction to give a product containing the  $\alpha,\beta$ -dicarbomethoxyvinyl group, IVa, as well as *trans*-PtCl<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>Q<sub>2</sub> (V), *cis*-PtCl<sub>2</sub>Q<sub>2</sub> (VI), and small amounts of dma oligomers. The oligomers and free dma were removed by washing with H<sub>2</sub>O, VI was removed by chromatography, and IVa was isolated from V by fractional crystallization. The overall reaction is therefore described by eq 1 and 2a.



The <sup>1</sup>H nmr spectrum (in CDCl<sub>3</sub>) of IVa shows the -CO<sub>2</sub>CH<sub>3</sub> signals at  $\delta$  3.66 and 3.48 as two singlets, the upfield signal having satellites due to coupling with <sup>195</sup>Pt ( $J_{\text{PtH}} = 3.0$  Hz). The phosphine-methyl signals at  $\delta$  1.83 and 1.76 appear as two overlapped triplets ( $^{2+4}J_{\text{PtH}} = 7.8$  and 8.0 Hz) with <sup>195</sup>Pt satellites ( $J_{\text{PtH}} = 27.6$  and 30.8 Hz, respectively) showing that the phos-

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