Table I

Compd	$(J_{AX} + J_{BX})$, Hz
I	7.88
II	8.98
2-Phenylcyclohexanone	16.75
2-Phenylcyclohexanone oxime (anti)	13.96
trans-2,6-Diphenylcyclohexanone	13.10
cis-2,6-Diphenylcyclohexanone	17.56
III (R = H)[a]	9.0
trans-2,6-Diphenylcyclohexanone oxime	
Syn proton	7.56
Anti proton	16.86
cis-2,6-Diphenylcyclohexanone oxime[b]	
Syn proton	7.69
Anti proton	11.22

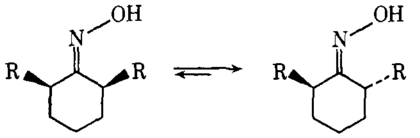
[a] Reference 2. [b] We believe that the low values observed here are due to distortion in the cyclohexylidene ring arising from the strong interaction between the hydroxyl group and the C-2 phenyl ring. An attempt is being made to determine the exact structure of this oxime by means of X-ray analysis.

In benzene-d_6 the nmr spectrum of I shows two sets of aromatic resonances centered at δ 7.08 and 7.49, each having narrow frequency distributions. Decoupling the benzylic proton causes pronounced multiplicity changes in the upfield aromatic signals showing them to be associated with the phenyl group on the cyclohexylidene ring. Double irradiation of the low-field group results in a 15.9% enchancement in the integral of the benzylic resonance. This NOE could only be observed if the C-2 hydrogen is dominantly equatorial. No such effect is observed with II (R = OAc) as might be anticipated, since the acetate hydrogens are too remote from the benzylic hydrogen in question.

Both I (R = Ac) and II (R = Ac) were submitted for X-ray structure determination. Gratifyingly, but as we expected, both compounds, as can be seen from the accompanying communication,[10] have (1) the C-2 phenyl group *in a perfectly axial orientation* and (2) *an alicyclic ring that is relatively strain free.*

Thus both in solution and in the solid state our evidence points conclusively to Ia and IIa *as the stable conformations* for these molecules, respectively.

Due to the instability associated with compounds such as III we did not attempt X-ray or further nmr analyses. Instead we chose to examine, by way of close analogy, the thermodynamic equilibrium between the oximes IV and V in which R is either methyl or phenyl.[11] The results of these equilibrations[12] (Table II) are quite dramatic in that *in each case the trans isomer V having an axial phenyl group is the more stable.* By simple calculation (based on average figures) one can calculate[13] that the OH–CH$_3$ nonbonded interaction is $\sim$2.5 kcal/mol[14] and that for IV (R = Ph) the OH–Ph interaction is[15] $\sim$5 kcal/mol.[14] We also believe that this latter value must approximate the OAc–2-Ph interaction in Ib. With regard to III (R = alkali metal) we consider that the equilibrium IIIb $\rightleftarrows$ IIIa should be even further to the right than that for IV $\rightleftarrows$ V (R = Ph), since not only is O^- intrinsically larger than O but it is attended by a gegenion and a solvent shell both of which might be expected to increase the steric bulk of the acinitro group *in toto*, as has been shown in the case of enolate anions.[16] Other results in support of the above conclusions will be reported later.



IV V

Table II

Starting oxime	% IV at equilibrium	% V at equilibrium
IV (R = CH$_3$)	18.0	82.0
V (R = CH$_3$)	19.7	80.3
IV (R = Ph)[a]	8.9	91.1
V (R = Ph)	5.8	94.2

[a] The nmr integration in this case was complicated by the presence of a small impurity whose absorption resonance overlapped that of the benzylic proton, rendering accuracy difficult. Thus, we believe that the values reported for the trans isomer (V, R = Ph) are the more accurate.

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(10) F. P. van Remoortere and J. J. Flynn, *J. Amer. Chem. Soc.*, **93**, 5932 (1971).

(11) The structures of all new compounds appearing in this paper and the relationship between the oximes and their corresponding ketones have been proven rigorously by chemical and physicochemical means.

(12) Equilibrations were carried out at 80° in ethanol for 3 weeks using a small amount of hydroxylamine acetate as the catalyst. In the cases where R = CH$_3$ small amounts of 2,6-dimethylcyclohexanone were found in the final mixture (analyzed by glc) but in those cases where R = Ph the oximes were recovered quantitatively and estimated by nmr.

(13) Based on data derived from 2,6-dialkylcyclohexanone equilibria [B. Rickborn, *J. Amer. Chem. Soc.*, **84**, 2414 (1962)].

(14) These values are approximate because the $-\Delta G_X°$ values of ref 13 and 15 refer to room temperature whereas our equilibria were determined at 80°.

(15) A $\Delta G_X°$ for phenyl = 3.1 was used, as reported by E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison in "Conformational Analysis," Interscience, New York, N. Y., 1965, p 44.

(16) S. K. Malhotra and F. Johnson, *J. Amer. Chem. Soc.*, **87**, 5513 (1965).

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Direct Proof of the Molecular Conformation of the Geometrical Isomers of α-Acetoxy-α,2-diphenyl(methylenecyclohexane)*

Sir:

In the preceding communication Johnson and Dix[1] have discussed the ground-state conformations of methylenecyclohexanes substituted at, and allylically to, the double bond, and of 2-substituted cyclohexanenitronate ions. Their equilibrium studies and analysis of nmr spectra are consistent only with a conformation in which the 2-phenyl substituent assumes an axial position in solution, as required by Johnson and Malhotra's theory of A$^{(1,3)}$ strain.[2]

In a supportive effort single-crystal X-ray diffraction studies of the α,α-disubstituted 2-phenyl(methylene-

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(1) F. Johnson and D. T. Dix, *J. Amer. Chem. Soc.*, **93**, 5931 (1971).

(2) F. Johnson and S. K. Malhotra, *ibid.*, **87**, 5492 (1965).

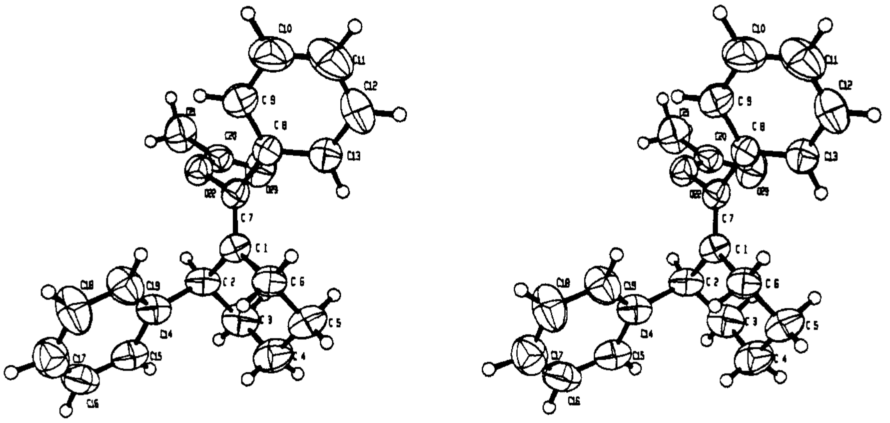


Figure 1. Three-dimensional view of *anti*-α-acetoxy-α,2-diphenyl(methylenecyclohexane) showing ellipsoids of thermal motion drawn at 50% probability.

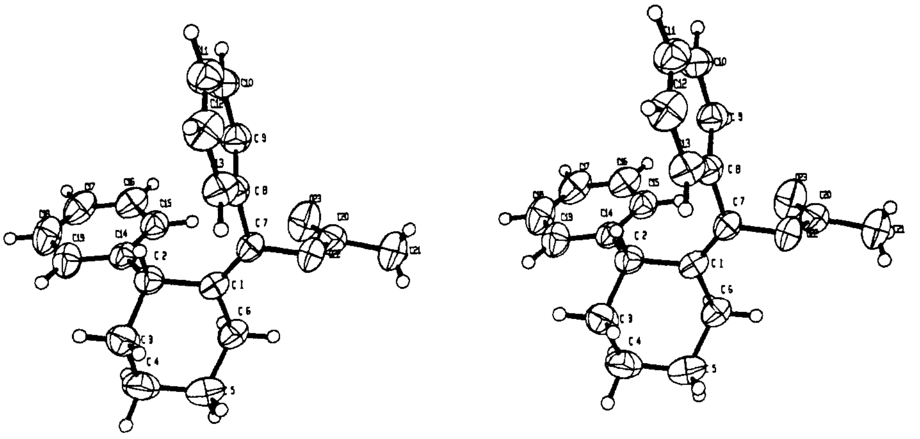
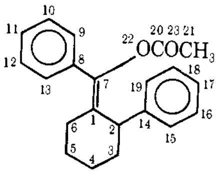


Figure 2. Three-dimensional view of *syn*-α-acetoxy-α,2-diphenyl(methylenecyclohexane) showing ellipsoids of thermal motion drawn at 50% probability.

cyclohexanes) were undertaken to determine the ground-state conformations in the solid state. We describe below the unambiguous identification of the stereochemical features of the geometrical isomers I and II of α-acetoxy-α,2-diphenyl(methylenecyclohexane).



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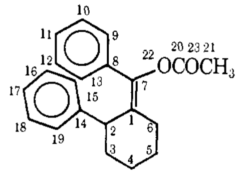

II

The two crystal structures were determined by very similar techniques, and their essential parameters as obtained in our experiments are summarized in Table I. A Picker four-circle diffractometer was used to determine the lattice constants and to gather intensity data in the θ–2θ scan mode using Ni-filtered Cu Kα radiation (λ 1.5418 Å). The structures were solved by the symbolic addition procedure[3] using the program MAGIC,[4] and refined by full-matrix least squares assuming anisotropic thermal parameters for C and O, and isotropic temperature factors for H. No corrections

Table I. Crystal Data

	I	II
Mol formula	$C_{21}H_{22}O_2$	$C_{21}H_{22}O_2$
Mol wt	306.408	306.408
Crystal habit	Tabula	Platelet
Major faces	{1, 0, 0}	{0, 1, 0}
Crystal size (mm)	0.12 × 0.20 × 0.33	0.93 × 0.30 × 0.09
Long direction	*c*	*a*
Space group	*Pbca*	$P2_1/c$
Cell constants (25°)	*a* 24.157 ± 0.006 Å	13.268 ± 0.008 Å
	b 16.758 ± 0.004 Å	16.887 ± 0.013 Å
	c 8.535 ± 0.002 Å	8.171 ± 0.006 Å
	β 90.0°	111.85 ± 0.03°
Unit cell volume ($Å^3$)	3455.4	1699.2
Density (calcd) (g cm^{-3})	1.178 (Z = 8)	1.198 (Z = 4)
Linear absorption coeff (cm^{-1}, Cu Kα)	5.91	6.01
No. reflections measured	2929	2878
No. reflections above background	1722	2222
$R_1 = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.065	0.054
$R_2 = \{\Sigma w[F_o - F_c]^2/\Sigma wF_o^2\}^{1/2}$	0.049	0.050

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(3) H. Hauptman and J. Karle, "Solution of the Phase Problem, I. The Centrosymmetric Crystal," ACA Monograph No. 3, Polycrystal Book Service, Pittsburgh Pa.

(4) The FORTRAN package MAGIC is written by R. B. K. Dewar and A. Stone, The University of Chicago, Chicago, Ill., and allows the application of the symbolic addition procedure to centrosymmetric crystals.

were made for absorption or anomalous dispersion, but a secondary extinction correction was applied.

The molecular geometry and the numbering system are shown in three-dimensional stereopair diagrams in Figures 1 and 2 for I and II, respectively. In both molecules the cyclohexylidene system adopts the familiar chair conformation whereby the 2-phenyl substituent assumes the axial position required by the theory of $A^{(1,3)}$ strain.[2] That these chairs conform closely to the geometry reported[5-7] for cyclohexane and its substituted derivatives is indicated by the average torsion angles about the C–C bonds (55.3 and 53.5° for I and II, respectively) which are within the range (52.9–57.1°) observed for cyclohexane derivatives.[5-7] The spread of their individual values in I, from 54.2 ± 0.4 to 56.8 ± 0.4°, is not larger than in disubstituted cyclohexanes,[7] but some distortions from "normal" chair geometry may be present in II, where the torsion angles range from 49.0 ± 0.3 to 59.6 ± 0.3°. The average internal bond angles at sp^3-hybridized carbon atoms (110.7 and 111.1° for I and II, respectively) compare well with values observed for cyclohexanes.[5-8] The internal C(2)–C(1)–C(6) angles at the sp^2-hybridized carbon atoms are 114.0 ± 0.3° for I, and 115.0 ± 0.2° for II.

In both isomers the axial phenyl group lies symmetrically above the ring in a manner which minimizes the nonbonded interactions between its ortho hydrogen atoms and the 4- and 6-axial hydrogens of the cyclohexylidene system (1,3-diaxial interactions). This geometry allows an ortho hydrogen atom to approach the 3-equatorial hydrogen fairly closely however, and results in contacts of 2.07 ± 0.04 Å for H(15)···H(32) in I, and 2.07 ± 0.03 Å for H(19)···H(32) in II.

An interesting difference in bond lengths occurs for the two types of C(sp^2)–O single bonds in these structures: the C(20)–O(22) bonds average 1.365 Å and apparently contain double character. They are substantially shorter than the C(7)–O(22) bonds which average 1.424 Å. The latter value might represent a good approximation to the C(sp^2)–O single bond since conventional resonance structures exclude double character in these bonds. Also, certain differences in conformation occur between I and II. C(7) is nearly coplanar with the acetoxy group in both molecules, and these planes form an angle of 81° in I and 88.9° in II with the planes are defined by {C(1), C(7), O(22)}. Although O(23) is cis to C(7) in both syn and anti isomers, twisting around C(7)–O(22) is in the opposite sense so that the acetoxy group is rotated toward the axial side of the cyclohexylidene system in I, but toward its equatorial side in II. The phenyl substituted at the double bond and the plane defined by {C(1), C(7), and C(8)} are not coplanar, but form a dihedral angle of 45.5° in I and 88.5° in II. The C(7)–C(8) bond lengths (1.471 ± 0.004 and 1.484 ± 0.003 Å for I and II, respectively) reflect the resulting absence of conjugation between the double bond and the aromatic system.

Small but significant distortions from planarity are observed in the unsaturated system formed by the exocyclic double bond. These distortions, which originate partly from nonplanarity at C(1) and C(7), and partly from twisting around the double bond, relieve nonbonded interactions of C(8) and O(22) with equatorial hydrogen atoms at C(2) and C(6), and will be discussed in detail in a future publication. Even further separation of C(8) and the 6- or 2-equatorial hydrogen is achieved by opening the C(1)–C(7)–C(8) angle to 130.1 ± 0.3 and 127.7 ± 0.2° in the anti and syn isomers, respectively.

Acknowledgment. We wish to thank Francis Johnson for suggesting the problem and supplying the crystals, and F. Peter Boer for helpful discussions.

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(5) J. D. Dunitz and P. Strickler, *Helv. Chim. Acta*, **49**, 2502 (1966).

(6) J. D. Dunitz and P. Strickler, *ibid.*, **49**, 2505 (1966).

(7) F. P. van Remoortere and F. P. Boer, *J. Chem. Soc.*, in press.

(8) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).

Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. VIII. Deuterium Isotope Effects in the Bond Reorganizations of Tricyclo[4.1.0.0^{2,7}]heptanes[1]

Sir:

Previously, structural considerations were advanced in support of the hypothesis that interaction of Ag^+ with bicyclobutanes leads in certain cases to argento carbonium ions. This particular mechanism, which requires the rupture of one edge bond and the central bond, was considered to be competitive with an alternative pathway involving the stepwise cleavage of two diametrically opposed edge bonds. The anticipated dependence of these carbonium ion mechanisms on appropriate incremental alkyl substitution of the bicyclobutane ring is most strikingly exhibited by tricyclo[4.1.0.0^{2,7}]heptane derivatives. For example, whereas **1a** gives rise quantitatively to *cis,cis*-1,3-cycloheptadiene (**2a**),[2,3] monomethyl derivative **3a** produces in 96% yield a mixture of four isomeric hydrocarbons when treated similarly with $AgClO_4$ in benzene at 40°.[1] We have presently obtained deuterium isotope effect data on **1** and **3** which now make manifest the intimate details of these bond reorganizations.

Whereas the rearrangement of **1a** at 40° in an azeotropically dried benzene solution of silver perchlorate (0.0845 *N*) proceeded with a rate constant of $2.27 \pm 0.03 \times 10^{-3}$ *M* sec^{-1}, its dideuterio analog **1b** exhibited a substantially *faster* rate of isomerization ($2.68 \pm 0.01 \times 10^{-3}$ *M* sec^{-1}), thereby giving rise to an *inverse* isotope effect (Table I). Similar rearrangement of **3a**

Table I. Deuterium Isotope Effect Data

Tricycloheptane	Product	k_H/k_D
1	**2**	0.847
3	**4** and **5**	0.95
	6	0.91
	7	1.74
3′	**4′** and **5′**	1.21
	6′	0.99
	7′	1.03

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[1] For paper VII of this series, see L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, **93**, 2335 (1971).

(2) (a) L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *ibid.*, **92**, 7002 (1970); (b) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **93**, 1288 (1971).

(3) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *ibid.*, **93**, 1043 (1971).