

and uranyl oxalate. The triple compartment cell was used for filter solutions. The filter solution combinations used and transparent wave length regions were as follows:

For the *m*- and *p*-nitrophenyl trityl ethers: cell I, solution of 63.5 g. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ /500 ml. of water; cell II, 68.6 g. of $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ /500 ml. of water; cell III, 38.8 g. of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ /500 ml. of water. This system was transparent between 290 and 360 μ .

For *p*-cyanophenyl trityl ether: cell I, solution of 76.2 g. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 82.3 g. of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ /600 ml. of water; cell II, 0.0372 g. of quinoline hydrochloride/liter; cell III 1.00 g. of 2,7-dimethyldiaza(3,6)cycloheptadiene-1,6 perchlorate/600 ml. This filter combination was transparent between 240 and 270 μ .

For *m*-cyanophenyl trityl ether: cell I, 127.0 g. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ /liter; cell II, 137.0 g. of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ /liter; cell III, 0.0366 g. of acridine hydrochloride/500 ml. of 1% hydrochloric acid. This filter combination was transparent in the region 265–320 μ .

In these quantum efficiency runs photolysis was continued to less than 20% reaction. Products were isolated in the same fashion as described in the preparative runs and quantum yields determined from the amount of product formed relative to the amount of light available with the given filter during the time of photolysis. Production of phenolic products was monitored

by titration. Light availability through each filter for the time of photolysis was determined using uranyl oxalate and potassium permanganate titration. The assumption²⁵ was made of 0.55 $\mu\text{mole}/\text{mmole}$ of oxalic acid utilized.

Calculations.—The calculation on the isomeric nitroanisoles was carried out by the simple LCAO MO method with neglect of overlap. Diagonalization of the secular determinant was by the Jacobi method using a Control Data Corp. 1604 computer.²⁶

Acknowledgment.²⁷—Appreciation is expressed by the authors for the support of this research by the Alfred P. Sloan Foundation and by the National Science Foundation. Similarly, appreciation is expressed for support of computing in this research by the Research Committee of the Graduate School of the University of Wisconsin from funds supplied by the Wisconsin Alumni Research Foundation.

(25) C. R. Masson, V. Boekelheide and W. A. Noyes, Jr., "Techniques of Organic Chemistry," Vol. II, Second Ed., Interscience Publishers, Inc., New York, N. Y., 1956, Chapter V.

(26) We thank Mr. John Munch for his assistance in computing.

(27) Thanks are due Mr. Gary A. Zimmerman for proof-reading the present manuscript.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINN.]

Conformations. III. Estimation of Rotational Conformations of Phenyl in Substituted 1-Phenylcyclohexenes by Proton Magnetic Resonance

BY EDGAR W. GARBISCH, JR.¹

RECEIVED APRIL 14, 1962

Phenyl rotational conformations in twenty substituted 1-phenylcyclohexenes have been estimated by the interrelation of olefinic proton chemical shifts and dihedral angles ϕ (in I) using theoretical values of Johnson and Bovey for shieldings experienced by a nucleus in the neighborhood of a benzene ring. It was found that practically identical results were obtained when the point dipole approximation method was used.

Waugh and Fessenden² have experimentally estimated that the magnetic anisotropy of the benzene ring³ leads to a chemical shift (δ) of -1.50 p.p.m. (deshielding) for the benzene proton magnetic resonance. From this chemical shift, a spacing of 1.28 Å. between the maximum π -electron density of the two circular π -electron clouds in benzene was found.^{4,2} Using this model, Johnson and Bovey⁴ have calculated the magnetic field (resulting from the magnetically induced precession of three π -electrons in each of the circular loops) about a freely tumbling benzene ring in an external magnetic field. The Johnson and Bovey tables⁴ provide theoretical chemical shifts for protons in the neighborhood (in terms of coordinates ρ and z) of the benzene ring. For simple aromatic hydrocarbons agreement between theory and experiment is good.⁴

Non-coplanarity of conjugated systems is readily detectable through ultraviolet spectroscopy. The effects of non-coplanarity upon the spectra of conjugated systems are varied.⁵ The intensity of absorption (or more reliably the oscillator strength) is generally considered to be uniformly more sensitive to deviations from coplanarity of the conjugated system than is the transition energy^{5,6}; however, this generality is neither theoretically⁷ nor experimentally⁸ without exception.

(1) (a) N.S.F. Postdoctoral Fellow, 1961–1962. Present address: Department of Chemistry, University of Chicago, Chicago 37, Ill. (b) Paper I and II in this series, *J. Org. Chem.*, **27**, 4243, 4240 (1962).

(2) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957); see also correction by J. S. Waugh, *ibid.*, **80**, 6697 (1958).

(3) L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936); and J. A. Pople, *ibid.*, **24**, 1111 (1956).

(4) C. E. Johnson, Jr., and F. A. Bovey, *ibid.*, **29**, 1012 (1958).

(5) W. F. Forbes, "Steric Effects in Conjugated Systems," Academic Press, Inc., New York, N. Y., 1958, p. 62.

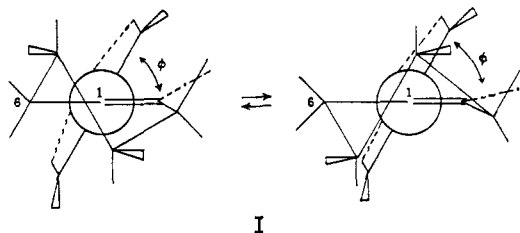
(6) M. J. S. Dewar, *ibid.*, p. 46; W. F. Forbes and R. Shilton, *J. Am. Chem. Soc.*, **81**, 786 (1959); E. Heilbronner and R. Gerdil, *Helv. Chim. Acta*, **39**, 1996 (1956).

(7) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **68**, 601 (1955).

(8) W. F. Forbes and W. A. Mueller, *J. Am. Chem. Soc.*, **79**, 6495 (1957).

Recently,⁹ simple LCAO–MO theory has been used to correlate the interplanar angle in biphenyls,^{9a} stilbenes and styrenes^{9b} with the wave length of maximum absorption.

This paper concerns itself with an estimation of the time-averaged dihedral angles (ϕ)^{10a} in *C*₆- and *ortho*-substituted 1-phenylcyclohexenes (I) through chemical shifts of the olefinic proton's magnetic resonance.^{10b}



Model and Anisotropy Calculations.—The cyclohexene model used is that derived from vector analysis by Corey and Sneen¹¹ in which total distortion (from normal tetrahedral) in all angles is approximately equal and as small as possible. The angle between each vinyl bond and the carbon–carbon double bond is taken as 122.5°. Bond lengths taken are: 1.54 Å. (C–C), 1.09 Å. (C–H), 1.48 Å. (C_{olefinic}–C_{Ar}),

(9) (a) H. Suzuki, *Bull. Chem. Soc. Japan*, **32**, 1340, 1350, 1357 (1959); (b) **33**, 619 (1960), and references cited therein.

(10) (a) In this work, ϕ is not to be distinguished from $-\phi$ (the supplement of ϕ); (b) I. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 125 ff., has suggested a similar treatment for the substituted biphenyls. See also: M. Katayama, S. Fujiwara, H. Suzuki, Y. Nagai and O. Simamura, *J. Mol. Spectry.*, **5**, 85 (1960).

(11) E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **77**, 2505 (1955). In Fig. 3 of this work, the *y*-coordinate for allylic axial substituents at both *a* and *d* was taken as -0.175 in place of -0.175 and 0.175 , respectively, as reported. The *y*-coordinate for allylic equatorial substituents at both *a* and *d* was taken as 0.109 in place of 0.109 and -0.109 , respectively, as reported. This typographical error has been confirmed by Professor Corey.

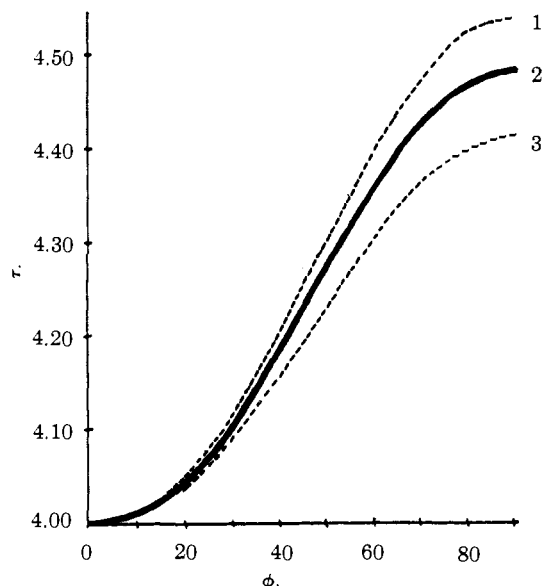


Fig. 1.—Theoretical τ -values for the olefinic proton of 1-phenylcyclohexene as a function of dihedral angle ϕ . Curves 1, 2 and 3 result from taking trigonal angles of 120, 122.5 and 125°, respectively.

1.33 Å. (C=C) and 1.39 Å. (aromatic C—C).¹² All distances used for anisotropy calculations were obtained by means of standard trigonometric procedures and, when applicable, appropriate coordinates given by Corey and Sneen.¹¹ Distances taken for carbon-carbon single bond shieldings are from the proton to the center of the appropriate C—C bond. The carbon-carbon single bond shieldings (σ) in p.p.m. were calculated using equation 1,¹³ and taking 8.3×10^{-30} cm.³/molecule as equal to $(\chi_L - \chi_T)$.¹⁴ To obtain σ for shieldings of the olefinic proton by the C_{Ar}—CH₃ bond in 1-*o*-tolylcyclohexene at any dihedral angle ϕ (see I), γ and R (in Å.) were calculated using eq. 2 and 3, respectively. The benzene shieldings in p.p.m. for values of cylindri-

$$\sigma = \frac{(1 - 3 \cos^2 \gamma)(\chi_L - \chi_T)}{3R^3} \quad (1)$$

$$\cos \gamma = \frac{2.57 - 7.90 \cos \phi}{4.11(12.12 - 7.90 \cos \phi)^{1/2}} \quad (2)$$

$$R = (12.12 - 7.90 \cos \phi)^{1/2} \quad (3)$$

$$\rho = (2.31 \cos^2 \phi + 5.04)^{1/2} \quad (4)$$

$$z = 1.52 \sin \phi \quad (5)$$

cal coordinates ρ and z (expressed in units of ring radii) were obtained from the Johnson and Bovey tables.⁴ Coordinates ρ and z as a function of dihedral angle ϕ (see I) are represented by eq. 4 and 5, respectively. In all calculations it is assumed that no deformation of the cyclohexane model (chair) or aromatic system results upon substitution, or upon twisting of the aromatic system about the central bond (C₁—C_{Ar} in I). The central bond length is taken as 1.48 Å. for all dihedral angles ϕ .

Results

Taking trigonal angles C=C—H and C=C—Ar to be 122.5° and constant, chemical shifts for the olefinic proton were calculated from the Johnson and Bovey tables⁴ to vary from -0.506 p.p.m. to -0.024 p.p.m. ($\delta = 0.48$ p.p.m.) as the dihedral angle ϕ varies from 0° to 90°, respectively. Providing an angle ϕ can be assigned to the reference compound, 1-phenylcyclohexene, the values of ϕ

(12) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, appendix.

(13) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(14) J. I. Musher, *ibid.*, **35**, 1159 (1961).

resulting from substitutions on C₆ or *ortho*-C_{Ar} can, in theory, be calculated.

The interplanar angle in biphenyl in solution at a temperature of about 25° is thought to be about 20° to 30°.^{9a,15} Because both steric repulsion energy (*ortho* hydrogens) and resonance energy decrease as the interplanar angle increases from 0°, the sum of these two energies is found essentially to balance one another from angles 0° to 30°, giving a plateau in the potential energy function with a small minimum at about 20° to 25°. This balance of steric and resonance energies is thought to be offset at a smaller angle ϕ in 1-phenylcyclohexene, since steric repulsion energy from *olefinic* and *ortho* hydrogens decreases and that from *allylic* and *ortho* hydrogens may increase as ϕ increases from 0°. This may give a near balance in total steric repulsion energy over small angles with the sum of steric and resonance energies exhibiting a minimum at an angle close to 0°. This point turns out to be not so critical, because should the benzene ring in 1-phenylcyclohexene be permitted to oscillate freely about $\phi = 0^\circ$ by 30°, the resultant chemical shift for the olefinic proton would differ from that for $\phi = 0^\circ$ (rigid) by only 0.03 p.p.m. Since the experimental uncertainty in tau value measurements is ± 0.02 p.p.m., it is felt that an arbitrary assignment of 1-phenylcyclohexene to an approximately planar conformation ($\phi = 0^\circ \pm 20^\circ$) is justifiable.

Taking the observed tau values of 4.00 for the olefinic proton of 1-phenylcyclohexene as representative of ϕ equal to zero, curves 1, 2 and 3 in Fig. 1 show theoretical τ -values as a function of ϕ for trigonal angles equal to 120°, 122.5° and 125°, respectively. The solid curve in Fig. 1 describes the equation $\tau = 4.00 + 0.482 \sin^2 \phi$ within ± 0.02 p.p.m. It is seen that τ -values for all curves do not vary significantly for $\phi = 0^\circ$ to 15° and 75° to 90°, and that $d\tau/d\phi$ is largest between $\phi = 15^\circ$ to 75°. This is convenient, not only because of the uncertainties described for the reference compound, but also because intermediate angles are of primary interest and these values will be obtained with a larger degree of certainty. Figure 1 shows that should the two assigned trigonal angles of 122.5° be in error by $\pm 2.5^\circ$ (total of $\pm 5^\circ$), an uncertainty in ϕ no greater than $\pm 5^\circ$ results between $\phi = 0^\circ$ and 60°.

For the C₆- and *ortho*-substituted 1-phenylcyclohexene derivatives considered in this work (see Table I), a correction for the anisotropy and/or electronic effects of the substituents is needed in a number of instances. For the C₆-COCH₃ derivatives a correction of 0.26 p.p.m. is added to the observed tau values for the vinyl protons of 1-methylcyclohexene (4.68 τ)^{1b} and 6-acetyl-1-methylcyclohexene (4.42 τ)^{1b} is representative of the deshielding incurred by the olefinic proton from the acetyl function alone.^{16a} In the same

(15) C. A. Coulson, "Theoretical Organic Chemistry; The Kekulé Symposium," Butterworths Scientific Publications, London, 1959, p. 49; see also F. A. Adrian, *J. Chem. Phys.*, **28**, 608 (1958).

(16) (a) A referee has pointed out that should the conformational equilibrium constants of the C₆-substituents of the 6-substituted 1-methylcyclohexenes differ appreciably from those of the 6-substituted 1-phenylcyclohexenes, an uncertainty (unpredictable) would arise in the corrections under discussion. Qualitative estimation of the conformational equilibria of 6-nitro- and 6-acetyl-1-methyl (and phenyl) cyclohexenes have been made (see paper II of this series^{1b}). The nitro group was found to be largely axial and the acetyl group was found to have no preference for axial or equatorial positions in these derivatives. No similar comparison was made for the C₆-(2-hydroxy-2-propyl) derivatives; however, this group should differ little from the C₆-isopropyl or C₆-*tert*-butyl groups which were calculated to shield insignificantly (due to carbon-carbon single bond anisotropy) the olefinic proton (see text). The referees' point is well made particularly with reference to a number of derivatives thought to be conformationally homogeneous (no. 14, 19, and 20 Table I) and to several of the 6,6-disubstituted derivatives (no. 15 and 21, Table I). In these instances, because of the

manner, a correction of 0.51 p.p.m. is added to the olefinic τ -values for C_6 -NO₂ derivatives (1-methyl-6-nitrocyclohexane; 4.17 τ for the olefinic proton)^{1b} and 0.50 p.p.m. is added to the olefinic τ -value for 6-bromo-6-nitro-1-phenylcyclohexene (6-bromo-1-methyl-6-nitrocyclohexene; 4.18 τ for the olefinic proton).^{1b} For the C_6 -(2-hydroxy-2-propyl) derivatives, a correction of 0.06 p.p.m. is added to the olefinic τ -values, taking the allylic and C_4 -allylic protons of cyclohexene (8.04 τ)^{16b} and 2-cyclohexenol (7.98 τ),^{16b} respectively, as references. A correction of -0.04 p.p.m. is added to the τ -values for the olefinic protons for the various 4,4-dimethyl substituted derivatives (Table I). This is based on the $\Delta\tau$ for 4,4-dimethyl-1-phenylcyclohexene (4.04 τ) and 1-phenylcyclohexene (4.00 τ).^{1b,17} No correction was applied for C_6 -methyl, isopropyl, *tert*-butyl, dimethyl and diethyl substituents (Table I). Calculations show that shieldings probably would be inside experimental error unless deformations of the cyclohexene ring occur, in which case corrections would be indeterminable. The olefinic proton tau value for 4-*tert*-butyl-1-*p*-tolylcyclohexene is 0.03 p.p.m. to higher field as compared with that for 1-phenylcyclohexene (or 4-*tert*-butyl derivative).^{1b} This small shielding is attributable to an electronic (hyperconjugative) effect and will probably drop off to insignificant values as the phenyl is rotated out of coplanarity. This correction is not applied to the olefinic proton τ -values for the tolyl and xylyl derivatives investigated.

A correction for C_6 -phenyl is not as directly obtained. The predominating conformation for the 6-phenyl in 1,6-diphenylcyclohexene has been determined as axial.^{1b} The ultraviolet spectrum^{1b} of this compound is almost identical with that for 1-phenylcyclohexene (Table I). The tau value of the olefinic proton (3.71) for 1,6-diphenylcyclohexene is surprisingly low as compared with those for most of the alkenes investigated. This suggests that the olefinic proton is being largely deshielded by the C_6 -phenyl. There is one sharp absorption ($\bar{\nu}_H = 4$ c.p.s.) for the phenyl protons at 2.92 τ ^{1b} (these protons absorb at 2.83 τ for 1-phenylcyclohexene^{1b} and 2.88 τ for 2-phenylpropane^{16b}). This is taken to indicate that the protons of C_1 - and C_6 -phenyl are far removed from one another and experience slight over-all shielding. A model which is consistent with these observations has the C_1 -phenyl essentially planar and the C_6 -phenyl in a fairly confined rotational conformation¹⁵ with the olefinic proton nearly in the magnetic anisotropy of the groups involved, there may be significant error in the applied corrections. The consistency between the n.m.r. and ultraviolet spectral data (see Table I and text), however, suggests that the errors involved here are probably unimportant. (b) G. V. D. Tiers, "Tables of τ -Values for a Variety of Organic Compounds," Minnesota Mining and Manufacturing Co., Project 737602, 1958, St. Paul, Minn.

(17) The anisotropy of the 4,4-dimethyl grouping was calculated to have no significant effect on the olefinic proton (axial C-C shield by ca. 0.04 p.p.m. and equatorial C-C deshield by ca. 0.06 p.p.m.). The C-CH₃ bond in 4-methyl-1-phenylcyclohexene was calculated to deshield the olefinic proton by about 0.04 p.p.m. providing the methyl group occupies an equatorial position 80% of the time. The expected τ -value for the olefinic proton of this material is about 3.96. A value of 4.01 τ was observed.^{1b} The tau value of 4-*tert*-butyl-1-phenylcyclohexene was found to be the same as for 1-phenylcyclohexene (4.00 τ).^{1b} An explanation of these small discrepancies is not readily apparent.

(18) (a) D. Y. Curtin, H. Gruen, Y. G. Hendrickson and H. F. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961), have demonstrated the restricted rotation of the phenyl rings in *cis*-1,2-diphenylcyclopentane by showing a temperature dependence of the $\bar{\nu}_H$ for the phenyl-proton absorption band. (b) The low tau value of 8.64 for the 6-methyl in 1,6-diphenyl-6-methylcyclohexene as compared with that for the methyl in ethylbenzene (8.80)^{16b} suggests that in the former instance the methyl is maintained, for the most part, in the nodal plane of the C_6 -phenyl. The deshielding of the olefinic proton would not be changed significantly should the C_6 -phenyl exist in the quasi-equatorial conformation (ca. 0.16 p.p.m. for quasi-equatorial vs. 0.19 p.p.m. for quasi-axial). (c) The low tau value of 6.08^{1b} for the C_6 -proton of 1,6-diphenylcyclohexene may be accounted for in the following way. Taking -0.79 p.p.m. as the "inductive" shielding experienced by a methyl proton of 2-methylpropane upon exchange of isopropyl for phenyl (9.11

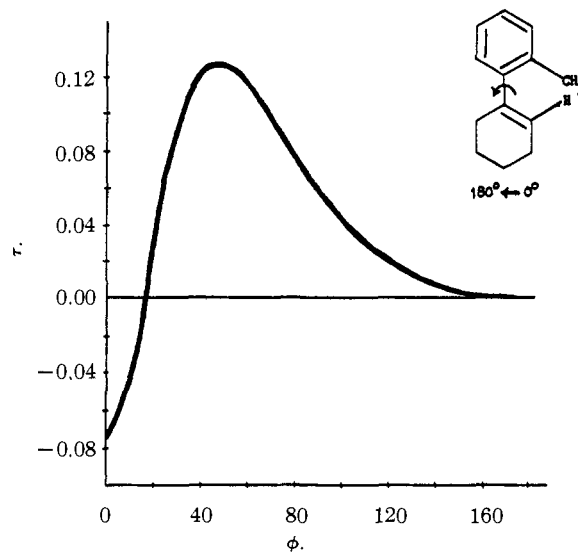
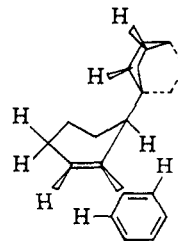


Fig. 2.—Chemical shifts in p.p.m. experienced by the olefinic proton, resulting from the CH_3 - C_{Ar} bond anisotropy, as a function of ϕ . The conformation represented in the upper right of the figure is taken as $\phi = 0^\circ$.

nodal plane of the ring (see II). Calculations show that for this model, the deshielding experienced by the olefinic proton will range from about 0.19 to 0.25 p.p.m. depending upon whether the phenyl is quasi-axial or axial, respectively. Adding these shifts to the observed value (3.71 τ) for the olefinic proton of 1,6-diphenylcyclohexene gives a corrected tau value of 3.90–3.96 τ which is reasonably close to the observed tau value of 4.00 τ for the olefinic proton of 1-phenylcyclohexene.



II

Taking these observations as justification, the angle ϕ of the C_1 -phenyl is assumed the same as that for 1-phenylcyclohexene ($0 \pm 20^\circ$). A correction of 0.29 p.p.m. is then applied to bring the tau values for the olefinic protons into agreement. The rotational conformation of the C_6 -phenyl in 1,6-diphenyl-6-methylcyclohexene (Table I) is taken to be the same as in II, and the correction of 0.29 p.p.m. is applied here.^{15b,c}

Allowance had to be made for the anisotropy of the C - C_{Ar} bond of 1-*o*-tolylcyclohexene. This was done by calculating chemical shifts for the olefinic proton brought about by the C - C_{Ar} bond as a function of dihedral angle ϕ over 180° , and taking the conformation with olefinic hydrogen and methyl opposed as $\phi = 0^\circ$ (see Fig. 2). These shifts were then added to the solid curve in Fig. 1 (over 180°) and the resulting curve (Fig. 3) was used to obtain angles ϕ . Similar

τ for methyl of 2-methylpropane vs. 8.32 τ for the vinylic methyl of α -phenyllandrene^{4,15b}, and exchanging phenyl for axial isopropyl of 6-isopropyl-1-phenylcyclohexene,^{1b} leads to a tau value of about 6.58 for the C_6 -proton of 1,6-diphenylcyclohexene (neglecting C_6 -phenyl anisotropy effects). Now applying the calculated deshielding experienced by the equatorial C_6 -proton (both for in the nodal plane and above the plane of the C_6 -phenyl) as a result of the C_6 -phenyl anisotropy (0.66 and 0.51 p.p.m., respectively), the tau value expected for the C_6 -proton of 1,6-diphenylcyclohexene lies between 5.92 and 6.07. This is in good agreement with the observed tau value of 6.08.

TABLE I
 DIHEDRAL ANGLES ϕ FOR SUBSTITUTED 1-PHENYLCYCLOHEXENES (I)^a

Cmpd.	Substituents	Olefinic proton τ		Angle ϕ	Pre-dominant conformation of C ₆ -subst. ^f	$\lambda_{\max}^{\text{MeOH}}$, m μ	log ϵ^g
		Obsd.	Corr. ⁱ				
1	None	4.00	4.00	0 ^{ob}	..	247	4.09
2	6-Methyl	4.21	4.21	43°	..	242	4.05
3	6-Isopropyl	4.21	4.21	43°	..	239.5	4.02
4	6- <i>tert</i> -Butyl	4.25	4.25	48°	ax.	239.5	4.00
5	6,6-Dimethyl	4.62	4.62	90°	..	227 ^j	3.65
6	6,6-Diethyl	4.40	4.40	66°	..	227 ^j	3.68
7	6-Phenyl	3.71	4.00 ^c	0 ^{oc}	ax.	246.5	4.05
8	6-Phenyl; 6-methyl	3.96	4.25	48°	..	240	3.99
9	<i>o</i> -Methyl	4.51	4.51	69°, 100 ^{od}	..	228 ^j	3.75
10	<i>o,o</i> -Dimethyl	4.60	4.60	90 ^{oe}	..	^e	^e
11	6-(2-Hydroxy-2-propyl)	4.14	4.20	42°	ax.	239.5	4.02
12	4,4-Dimethyl; 6-(2-hydroxy-2-propyl)	4.34	4.36	61°	eq.	236	4.01
13	6-Acetyl	3.89	4.15	36°	^k	244	4.05
14	6-Acetyl; 4,4-dimethyl	3.95	4.17	38°	eq.	244	4.09
15	6-Acetyl; 6-ethyl	3.94	4.20	42°	..	242	3.94
16	6-Nitro	3.66	4.17	38°	ax.	238.5	4.05
17	4- <i>tert</i> -Butyl; 6-nitro; <i>p</i> -methyl (<i>trans</i> isomer)	3.64	4.15	36°	ax.	246	4.13
18	4-Methyl; 6-nitro; (<i>trans</i> isomer)	3.63	4.14	35°	ax.	239	4.05
19	4-Methyl; 6-nitro (<i>cis</i> isomer)	3.86	4.37	62°	eq.	236	4.05
20	4,4-Dimethyl; 6-nitro	3.88	4.35	60°	eq.	236.5 ^h	4.05 ^h
21	6-Bromo; 6-nitro	3.92	4.42	70°	..	220-230 ^j	3.99-3.93

^a Tau values have a mean deviation of less than ± 0.02 p.p.m. ^b Assumed $0 \pm 20^\circ$; see text. ^c Arbitrarily adjusted to $0 \pm 20^\circ$; see text. ^d Taken from Fig. 3. ^e Taken from Fig. 4. ^f See ref. 1b. ^g No conjugation band. ^h Isooctane solvent. ⁱ See text. ^j Inflection. ^k No conformational preference.

allowances were made for 1-(2,6-dimethylphenyl)-cyclohexene resulting in the curve shown in Fig. 4 from which angle ϕ was extracted.

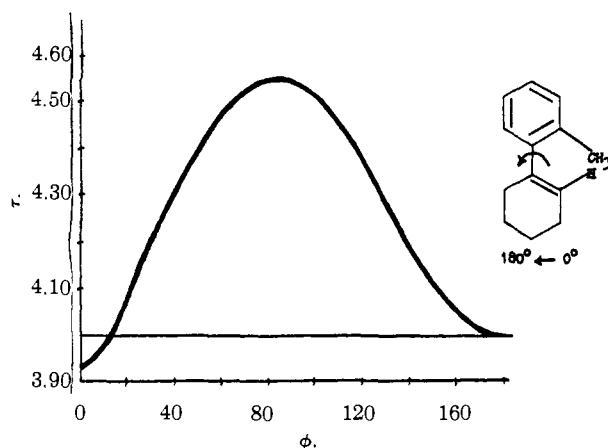


Fig. 3.—Theoretical τ -values for the olefinic proton of 1-phenylcyclohexene as a function of ϕ . Conformation represented in upper right of the figure is taken as $\phi = 0^\circ$.

Table I summarizes the results from the dihedral angle ϕ calculations. Ultraviolet spectral data are included for comparison.

Discussion

The data summarized in Table I are, as a whole, self consistent. The angles ϕ represent time-averaged values which may not coincide with the equilibrium dihedral angles, and which may be reliable to not better than $\pm 15^\circ$. The majority of the values of ϕ are found to lie between 35° and 70° , or within the preferred region of the solid curve in Fig. 1. It is seen that in only one instance (cmpd. 5) did an observed olefinic proton τ -value (corrected for substituent effects) fall outside the maximum or minimum limit for ϕ equal to 90° or 0° . 6,6-Dimethyl-1-phenylcyclohexene exhibits an olefinic proton signal which has a τ -value 0.14

p.p.m. higher than the maximum calculated value for $\phi = 90^\circ$. This is in contrast to the tau value of the olefinic proton of 6,6-diethyl-1-phenylcyclohexene (cmpd. 6) which falls within the calculated limits. The ultraviolet spectra of cmpd. 5 and 6 are very nearly the same (Table I). Whereas a definitive rationalization of this discrepancy cannot be offered at this time, it should be pointed out that the large non-bonded interactions which must be present particularly in the 6,6-disubstituted derivatives will be compensated for not

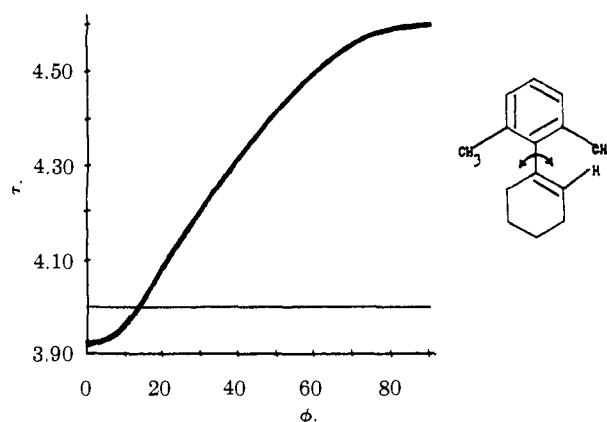


Fig. 4.—Theoretical τ -values for the olefinic proton of 1-(2,6-dimethylphenyl)-cyclohexene as a function of ϕ .

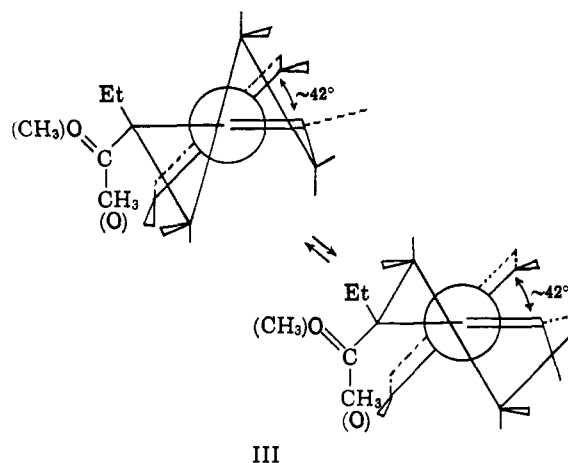
only by rotations about the central bond (C_1-C_{Ar}), but by distortions of bond angles and lengths, and by deformations of the cyclohexene ring system. Such occurrences will lead to shielding variations, not only from the aromatic system, but by the various carbon-carbon and carbon-hydrogen bonds.¹⁹

(19) Should the two trigonal angles ($C_1=C_2-H$) and $C_{Ar}-C_1=C_2$ vary from 122.5° by $\pm 2.5^\circ$ upon substitution (which leads to $\phi > 30^\circ$), the uncertainty in $\phi = 30^\circ$ is $\pm 5^\circ$, and this uncertainty decreases to an insignificant value as $\phi \rightarrow 90^\circ$. This shows that trigonal angle variances at large values of ϕ should not lead to large deviations from the solid curve in Fig. 1.

It was found that for the long-range shieldings of the olefinic proton by the phenyl which are dealt with in this work, the point dipole approximation¹³ leads to theoretical shieldings as a function of ϕ close to the values obtained from the Johnson and Bovey tables.⁴ For example, using eq. 1 and the experimental value of $(\chi_L - \chi_T)$ for benzene, -90×10^{-30} cm.³/molecule,²⁰ the shielding for $\phi = 0^\circ$ is -0.56 p.p.m. and that for $\phi = 90^\circ$ is -0.04 p.p.m. with a difference equal to 0.52 p.p.m. The Johnson and Bovey tables lead to a difference of 0.48 p.p.m. and comparable absolute shieldings (see earlier).

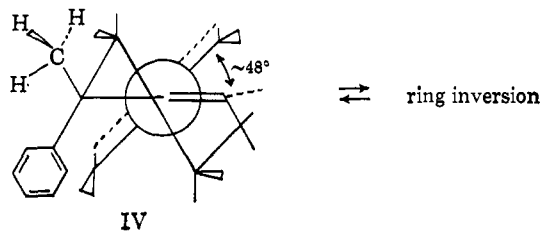
It is seen from Table I that equatorial C₆-(2-hydroxy-2-propyl) and C₆-nitro substituents (cmpd. 12, 19 and 20) appear to induce a larger angle ϕ than do the corresponding axially substituted analogs (cmpd. 11, 16, 17 and 18). This may also be construed^{1b} by comparing the ultraviolet spectra of these compounds which show a hypsochromic shift of about 3 m μ when the C₆-substituent occupies the equatorial as compared with the axial conformation (cmpd. 12 *vs.* 11; 19 and 20 *vs.* 16 and 18). No such effects become apparent upon comparing the C₆-acetyl compounds 13 and 14. These observations coupled with the finding^{1b} that there is little preference of the acetyl function in 6-acetyl-1-phenylcyclohexene (cmpd. 13) for either an axial or an equatorial conformation, whereas the nitro function in 6-nitro-1-phenylcyclohexane largely prefers the axial conformation, are consistent with the supposition^{1b} that the nitro function is acting in these instances as a larger group than is the acetyl function. This supposition is reasonable only if the barriers to rotation of the acetyl group in these compounds are large, thereby confining this group essentially to several rotational conformations of low non-bonded interactions,²¹ and if the nitro group is rotating more freely and as a result defining a relatively larger sphere of action.

Comparison of the ultraviolet spectra and angles ϕ for 6,6-dimethyl- and 6,6-diethyl-1-phenylcyclohexene with those for 6-acetyl-6-ethyl-1-phenylcyclohexene (cmpd. 5, 6 and 15, respectively) clearly indicates the phenyl to be rotated from the plane of conjugation to a larger extent in the former two compounds than in the latter compound. In addition, the data in Table I show that the angles ϕ for 6-methyl-1-phenylcyclohexene and 6-acetyl-6-ethyl-1-phenylcyclohexene are comparable. These data are compatible with a representation for cmpd. 15 in which the acetyl function is confined primarily to rotational conformations of least non-bonded interactions (see III). The low tau value of 7.89^{1b} for the acetyl methyl in cmpd. 15 as compared with 8.195 and 8.15 for those of 6-acetyl-1-phenylcyclohexene (cmpd. 13) and 6-acetyl-dimethyl-1-phenylcyclohexene (cmpd. 14), respectively,^{1b} is consistent with III. The benzene anisotropy may lead to a small deshielding of the acetyl



III

methyl protons in III and little influence (or slightly shield) those of cmpd. 13 and 14 in which the benzene ring is presumably rotated away from the C₆-acetyl function and in the direction of the C₆-proton. The acetyl functions in cmpd. 13 and 14 are likewise thought to occupy the rotational conformations shown in III. The large angle ϕ together with the ultraviolet spectrum of 6-bromo-6-nitro-1-phenylcyclohexene (cmpd. 21) as compared with these data for 6-acetyl-6-ethyl-1-phenylcyclohexene support the previous contention^{1b} that nitro is not restricted to select rotational conformations in this compound or in cmpd. 16-20.



IV

Using similar arguments as offered for support of III, the rotational conformations of C₁- and C₆-phenyl in 1,6-diphenyl-6-methylcyclohexene (cmpd. 8) are thought to be restricted and best represented as shown in IV. The complex proton magnetic resonance pattern for the benzene protons of this compound,^{1b} which exhibits signals at 414, 409, 403 and 392 c.p.s. (from tetramethylsilane), is not inconsistent with this representation.^{18a}

Experimental

Synthesis of the 1-phenylcyclohexene and 1-methylcyclohexene derivatives discussed in this paper, together with proton magnetic resonance (56.4 Mc./sec.) and ultraviolet spectral data, have been reported in papers I and II of this series.^{1b}

Acknowledgment.—The author is indebted to Professor Kreevoy for a number of profitable discussions, one of which led to the conception of the subject matter developed in this paper; and to Dr. W. B. Schwabacher for determining the n.m.r. spectra. The author is grateful for a postdoctoral fellowship from the National Science Foundation, and for an opportunity to discuss this work with Drs. F. A. Bovey and G. V. D. Tiers.

(20) C. Kittel, "Introduction to Solid State Physics," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 136-138.

(21) N. L. Allinger and M. A. DaRooge, *J. Am. Chem. Soc.*, **83**, 4256 (1961), have determined that the acetyl function of pregnane-20-one oscillates for the most part about a single conformation.