organic acid was isolated in 1.620 g yield (0.00953 mol or 83.3% from amide).

Hydratropic Acid-β-d_3. Acetophenone was reduced by lithium aluminum hydride in ether to yield α-hydroxyethylbenzene in 89.9% yield. The alcohol was converted to α-chloroethylbenzene by reaction with thionyl chloride in 89.8% yield. α-Cyanoethylbenzene was prepared from the chloride by reaction with sodium cyanide in dry dimethyl sulfoxide at 60° for 3 hr. The yield of α-cyanoethylbenzene was 85.4% from the chloride. The nitrile was hydrolyzed by refluxing in 33% aqueous potassium hydroxide for 24 hr to give α-methylphenylacetic acid in 97.8% yield. α-Methyl-d_3-phenylacetic acid was prepared from the analogous cyanide by hydrolysis in 99% D_2O. The cyanide was prepared, in the same manner as the protonated cyanide, from acetophenone-d_3, which was prepared by basic exchange of the acidic α protons of acetophenone in 99% D_2O at 100°. The deuterated α-methylphenylacetic acid contained deuterium at the α position. This was exchanged in basic water to yield α-methyl-d_3-phenylacetic acid, with 100% deuteration in the methyl position and no deuteration at other positions on the molecule, according to nmr analysis. α-Methylphenylacetic acid-α-d_1 was prepared from the protonated acid by exchange in basic 99% D_2O at 100°.

Phenylacetic acid-α,α-d_2 was prepared by basic exchange of the alpha protons in 99% D_2O at 100°.

Pivalic acid-d_9 was prepared by a Grignard sequence from *t*-butyl-d_9 chloride.

Kinetic Methods. The infrared and pseudo-first-order galvinoxyl methods for measuring the perester decomposition rates were previously described.[9]

The double-labeling method required preparation of solutions of the protonated, deuterated, and approximately 50:50 mixture of protonated–deuterated peresters in about 0.04 *M* concentration of perester and 0.12 *M* styrene with isooctane as solvent. A 50 ml solution was prepared out of which 20 ml was pipetted into each of two breakseal flasks for the "short" reaction time, with 5 ml put into each of two breakseal flasks for the "infinity" reaction time. The "short" reaction flasks were heated for 15–25% of total perester decomposition, the per cent of decomposition based on the infrared kinetic rate constants. The "infinity" reaction flasks were heated for ten half-lives to ensure complete decomposition of perester.

The breakseal flasks were opened on a vacuum line, and the volatile gases were allowed to expand into a mass spectrometer tube, with the breakseal cooled to −78°. The breakseal flask was closed off, and the volatile gases were condensed in the mass spectrometer tube at −200°. The only gases detectable from all the peresters except the pivaloyl were carbon dioxide and isooctane. Since isooctane does not give a fragment at mass peaks 44, 45, or 46, the ratios of 46/44 and 45/44 from carbon dioxide could be determined directly, without further purification of the carbon dioxide. The carbon dioxide from *t*-butyl perpivalate was contaminated with isobutane and isobutylene, which gave mass peaks at 45 and 46. The carbon dioxide was separated from all contaminants by chromatography at room temperature through a dibutyl phthalate column connected to a vacuum line, with helium as the carrier gas.

The 46/44 ratios for the protonated, deuterated, and mixed peresters for short and infinity reaction times were used to calculate the isotope effect directly. The denominator of the expression equals the ratio of the moles of protonated to deuterated weighed out initially times the ratio of the number of moles of carbon dioxide produced per mole of protonated perester to the number of moles of CO_2 produced per mole of deuterated perester (nH/nD). Since the initial weights of the two peresters in the mixture are known, the nH/nD ratio can be calculated.

Product Studies. The gaseous products from the decomposition were collected from breakseal flasks into a calibrated vacuum line. The total gas yield was thus obtained. The composition of the gas mixture was estimated by the sensitivities of the mass spectrometer to the components of the mixture. The only contaminant in the carbon dioxide produced from the decomposition of the phenylacetyl hydratropyl and cumyl peresters was isooctane.

Complete Conformational Analysis of 3-Phenylpropanol

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Abstract: The nmr spectrum of the aliphatic protons in $PhCH_2CH_2CH_2OH$ has been completely analyzed with the aid of various stereospecifically dideuterated derivatives. It is shown that the conformer with Ph, CH_2OH *trans* disposed is more stable than the *gauche* rotamer by 0.5 kcal mole^{-1}. In contrast, the rotamers with $PhCH_2$, OH *trans* and *gauche*, respectively, are about statistically populated. Two kinds of differential isotope effects on chemical shifts are noted.

We recently suggested an approximate method of conformational analysis of substituted ethanes[1] and demonstrated an unequivocal method of identifying the structure of the most stable conformer of some 1,1,2-trisubstituted ethanes.[2] As previously mentioned, our approach is applicable with greater validity to 1,2-disubstituted ethanes,[3] and in fact comparison of results derived from our simplified model with those from a more exact analysis seems quite favorable.[4] The explicit assumptions in our model as applied to the latter system are (1) that angular dependence of vicinal coupling constants follows a cos^2 function, $J = J_0 \cos^2 \phi$, and (2) all dihedral angles, ϕ, are 60° when substituents are *trans* but the angle is 65° when substituents are *gauche*. We showed[1] the energy differences calculated for 1,2-disubstituted ethanes is not particularly sensitive to the choice of dihedral angle near 60°, and further pointed out that conformational energy *differences* in the same compound as induced by changes in solvent should be reproduced quite well by this model. We report here on the application and results of our method to conformational analysis of 3-phenylpropanol (**1**), where the rotamer distribution about *both* bonds a and b, $PhCH_2\underset{a}{--}CH_2\underset{b}{--}CH_2OH$, has been determined and the most stable conformer has been identified. A later publication will deal with the conformational analysis of several 2-phenylethyl derivatives, of which this can be considered a member.

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[1] E. I. Snyder, *J. Am. Chem. Soc.*, **88**, 1165 (1966).

[2] M. Buza and E. I. Snyder, *ibid.*, **88**, 1161 (1966).

[3] See N. L. Allinger and coworkers, *ibid.*, **90**, 1199 (1968), for indication that one of the assumptions necessary for trisubstituted ethanes, but absent in the extension to 1,2-disubstituted ethanes, may not be generally applicable.

[4] G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *ibid.*, **89**, 1125 (1967).

Table I. Spectral Parameters for 3-Phenylpropanol[a]

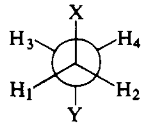
$$\underset{1}{\text{PhCH}_2}\underset{2}{\text{CH}_2}\underset{3}{\text{CH}_2}\text{OH}$$

Compound	Solvent	δ_{12}	J_{12}	$J_{12'}$	S_1[f]	S_2[g]	J_{23}
$PhCH_2CH_2CD_2OH$[b]	Methanol[d]	52.22	9.25	6.25			
	Pyridine[d]	49.3	9.32	6.21			
1:1 *erythro-*:*threo-* $PhCHDCHDCD_2OH$[c]	Carbon tetrachloride		9.18	6.63			
	Benzene		9.12	6.53			
	Acetonitrile		10.00	6.77			
	Acetone		9.76	6.58			
	Cyclohexane		9.03	6.62			
	Dimethyl sulfoxide		9.89	6.73			
threo-$PhCHDCHDCD_2OH$[b]	Methanol			6.24			
	Pyridine			6.26			
	Dimethyl sulfoxide			6.23			
	Benzene			6.41			
	Acetone			6.22			
threo-$PhCHDCHDCH_2OH$[b]	Carbon tetrachloride			6.34			
				$^1/_2\lvert J_{2'3} + J_{2'3'}\rvert = 6.50$			
				S[e] $= 19.39$			
erythro-$PhCH_2CHDCHDOH$[b]	Acetone				(12.64)		6.30
	Pyridine				(12.59)	7.59	6.20
	Carbon tetrachloride				(12.59)	7.51	6.24

[a] All parameters are in hertz. Concentrations are 20% weight volume unless otherwise noted. [b] Values are absolute, spectra having been taken on frequency-calibrated sweep widths. [c] Values are relative, spectra having been taken on uncalibrated sweep width. [d] Concentration is 40% weight volume. [e] S = separation between outermost components of $H_{2'}$. [f] $S_1 = \lvert J_{23} + J_{23'}\rvert$, and is the measured separation between the outermost components of the —CH_2O— triplet in $PhCH_2CH_2CH_2OH$. [g] S_2 = measured separation of the benzylic proton doublet.

For a 1,2-disubstituted ethane our approach[1] requires knowledge of the ratios of the vicinal coupling constants. Since complete spectral analysis of the six-spin system of the aliphatic protons in **1** seemed a tedious task, the simpler four-spin system of $PhCH_2CH_2CD_2OH$ was solved exactly and it was assumed that the two vicinal couplings about bond a were identical in the undeuterated and deuterated alcohol. Experimental support of this assumption comes from the observed self-consistency in couplings measured in variously deuterated samples of the title compound. Evaluation of the vicinal couplings about the b bond was made from the nmr spectrum of undeuterated alcohol and *erythro*-$PhCH_2CHDCHDOH$. The carbinol methylene group of **1** was a triplet under the resolution achieved. Although this appearance does not necessitate that the two vicinal couplings about bond b, J and J', be identical, one can equate the separation, S, between the outer lines of the triplet to the sum of these couplings with a high degree of accuracy, *i.e.*, $S = \lvert J + J'\rvert$. Since J (or J') is readily obtained by inspection from the spectrum of *erythro*-$PhCH_2CHDCHDOH$, then J' (or J) is determined because $\lvert J + J'\rvert$ is known. As will be mentioned several checks are available, all of which show a high degree of internal self-consistency.

Unequivocal identification of the most stable conformer of 1,2-disubstituted ethanes can be made by measuring the coupling in the stereospecifically dideuterated derivative, XCHDCHDY, if the configuration (*erythro* or *threo*) is known. The observed vicinal couplings, J_{13} and J_{14}, will be weight-averaged over the three conformers whose mole fractions are n_t and n_g,[5] giving $J_{13} = n_tJ_g + n_gJ_g + n_gJ_t$ and $J_{14} = n_tJ_t + 2n_gJ_g$. We assume that J_g, J_t are of the same sign and $\lvert J_t\rvert > \lvert J_g\rvert$. Since the two *gauche* conformers are enantiomers, $2n_g + n_t = 1$. Substitution for n_g and rearranging gives $\lvert J_{14}\rvert - \lvert J_{13}\rvert = \frac{1}{2}(\lvert J_t - J_g\rvert)(3n_t - 1)$. So, $\lvert J_{14}\rvert - \lvert J_{13}\rvert > 0$ so long as $n_t > 1/3$, the statistical population level. Therefore, if the *erythro*- and *threo*-dideuterio compounds are examined, in which case the sole vicinal couplings are $J_{erythro} = J_{14}$, $J_{threo} = J_{13}$, then the observation $J_{erythro} > J_{threo}$ implies that the *trans* conformer is the more stable. Since the sum, $\lvert J_{13} + J_{14}\rvert$, is readily available from spectra of the type AA'BB', it is necessary to prepare only one of the dideuterated diastereomers. If $J_{erythro}$ corresponds to the larger of the two vicinal couplings then the *trans* conformer is the more stable; if J_{threo} corresponds to the larger coupling then the *gauche* conformer is the more stable. This result is generally valid for all types of 1,2-disubstituted ethanes.[5]



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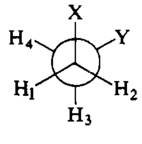

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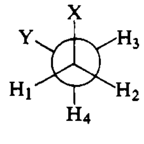

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Results and Discussion

The necessary deuterated species were synthesized as outlined in Scheme I. The diastereomeric nature of products is determined by the configuration of the preceeding olefin and is assumed to be the product of *cis* hydrogenation. This is known to be the case with high stereospecificity for styryl systems[6] and is assumed to be the preponderant course in other reductions. Our conclusions with regard to rotamer distribution about bond b turn out to be independent of the stereochemical course of hydrogenation of the enol acetate (*vide infra*). This is fortunate, since extensive scrambling accompanies reduc-

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(5) Although we treat the two gauche couplings, J_g, as identical, generally this is not so. However, our conclusions remain valid for all cases except those where $\lvert J_{12} - J_{13}\rvert$ becomes very small, *ca.* 0.5 Hz or less.

(6) G. V. Smith and J. A. Roth, *J. Am. Chem. Soc.*, **88**, 3879 (1966).

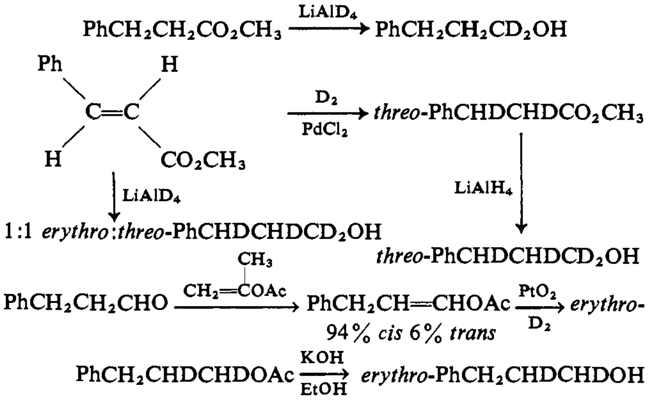
Table II. Conformational Energy Differences in $PhCH_2$–CH_2CH_2OH[a]

Solvent	E, kcal mole^{-1}
Carbon tetrachloride	0.48
Benzene	0.49
Cyclohexane	0.47
Acetonitrile	0.55
Acetone	0.56
Dimethyl sulfoxide	0.55
Methanol	0.56
Pyridine	0.57

[a] Calculated for 300°K from eq 5 of ref 1 using the data in Table I, the *trans* conformer being more stable in all cases.

tion and its stereochemical course is uncertain.

Scheme I



Complete analyses of AA′BB′ spectra were performed using the Reilly–Swalen program,[7,8] although $|J_{AB} + J_{AB'}|$ is readily measured from the separation of the $1S'_1 \rightarrow S_2$ and $S_{-2} \rightarrow 1S'_{-1}$ transitions.[9] All spectral parameters are listed in Table I.

Self-consistency of the parameters is demonstrated by the following checks. Analysis of $PhCH_2CH_2CD_2OH$ in pyridine and methanol affords values of $J_{12'}$ which are reproduced well by the measured coupling in *threo*-$PhCHDCHDCH_2OH$. The doublet separation of $C\mathit{H}_2O$ in *threo*-$PhCHDCHDCH_2OH$ is *ca.* $\frac{1}{2}|J_{2'3} + J_{2'3'}| = 6.50$ in carbon tetrachloride. However, the separation between the outermost lines of $C\mathit{H}DCH_2$ is *ca.* $|J_{2'3} + J_{2'3'} + J_{12'}| = 2(6.50) + 6.34 = 19.34$ Hz, calculated, whereas the observed separation is 19.39 Hz. In *erythro*-$PhCH_2CHDCHDOH$ the separation between outermost members of the benzylic proton "doublet" is *ca.* $\frac{1}{2}|J_{12} + J_{12'}|$, calculated to be 7.76 Hz in pyridine and observed as 7.59 Hz. Comparison of data in acetone and carbon tetrachloride is not possible because the individual couplings measured represent those from uncalibrated spectra.

That the sole coupling in *threo*-$PhCHDCHDCD_2OH$ is the smaller of the two couplings demonstrates unequivocally that the *trans* conformer about bond a is the more stable. Since in *erythro*-$PhCH_2CHDCHDOH$ $J_{23} \sim {}^1/_2S_1 = {}^1/_2|J_{23} + J_{23'}|$ this requires equality, or nearly so, of the latter vicinal couplings. This means that the rotamers about bond b are quite close to statistical distribution. Although this latter result may be surprising, we note that an hydroxyl group causes little conformational preference about the adjacent carbon–carbon bond in both CH_3CH_2–CH_2OH and $PhCH_2$–CH_2OH[10] and is consistent with Whitesides' data.[4] The conformational energy differences about bond a are listed in Table II.

The conformational energy difference in $PhCH_2CH_2CH_2OH$ is quite similar to that observed[10] in the parent hydrocarbon, $PhCH_2CH_2CH_3$. Therefore the hydroxyl group plays no important part in influencing the energetics of conformational equilibrium, as it might be expected to do if intramolecular hydrogen bonding to the aromatic ring were present. In fact Oki found no evidence for an intramolecular OH–Ph bond from infrared studies,[11] and independent examination in these laboratories confirms this.[12] One notes that the conformational energy differences are 0.47–0.49 kcal mole^{-1} in non polar solvents, but 0.55–0.57 kcal mole^{-1} in the polar, hydrogen-bonding solvents employed. This is readily understood if one pictures the latter group of solvents as effectively associating with the hydroxyl group, thereby increasing its effective "size" and displacing the equilibrium toward the *trans* conformer. In fact Munk has previously noted such an effect on rotamer distribution in molecules where intramolecular hydrogen bonding preferentially stabilized one of the conformers.[13] As might be anticipated the effect of solvent on conformer distribution is far larger in the latter case than in the present work.

Isotope Effects. The variously deuterated 3-phenylpropanols show two distinct kinds of deuterium isotope effects on chemical shift. Measurements on mixtures of *erythro*-*threo*-$PhCHDCHDCD_2OH$ consistently demonstrated that the *threo* diastereomer had a chemical shift difference between aliphatic protons 0.2 Hz less than the *erythro* isomer. Such a differential isotope effect on diastereomers seems to be a general phenomenon on which we have commented before.[14] Should such a differential isotope effect on chemical shift also obtain for C^{13} spectroscopy then the latter should prove to be an extremely convenient means of analysis of dideuterated diastereomers. From measurements in a 2:1 mixture of $PhCH_2CH_2CD_2OH$–*threo*-$PhCHDCHDCD_2OH$ in methanol δ_{12} was measured as 52.14 and 49.81 Hz respectively. This arose from a relative upfield shift of $PhC\mathit{H}D$ of 2.8_0 Hz and of $C\mathit{H}D$ of only 0.4_7 Hz, Therefore it is obvious that the magnitude of a deuterium isotope effect on chemical shift is an extremely sensitive function of environment. One cannot help but wonder what practical use such observations can serve.

Experimental Section

All nmr spectra were obtained on a Varian A-60 spectrometer

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(7) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

(8) The computational part of this work was carried out in the Computer Center of the University of Connecticut, which is supported in part by Grant GP-1819 of the National Science Foundation.

(9) J. A. Pople, W. G. Schneider, and H. S. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 144.

(10) T. Cheng and R. Jablonski, unpublished results.

(11) M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 1135 (1959).

(12) We thank Mr. Richard Weiss for performing the relevant ir work.

(13) M. E. Munk, M. K. Meilahn, and P. Franklin, *J. Org. Chem.*, **33**, 3480 (1968).

(14) R. J. Jablonski and E. I. Snyder, *J. Am. Chem. Soc.*, **90**, 2316 (1968).

system with sweep width calibration obtained by the audio sideband method. Deuterium irradiation was accomplished with an nmr specialities HD-60A decoupler.

3-Phenylpropanol-1,1-*d*$_2$. Reduction of methyl hydrocinnamate with lithium aluminum deuteride in ether in the usual manner afforded the title compound, which was purified by distillation, bp 75–78° (0.7 mm), containing 3% unreacted ester by glpc examination (10% diethylene glycol succinate, 150°).

***threo*-3-Phenylpropanol-1,1,2,3-*d*$_4$ and -2,3-*d*$_2$.** A solution of 8.1 g (50 mmoles) of methyl cinnamate in 100 ml of ethyl acetate containing 0.103 g of palladium chloride (0.58 mmole) was treated with deuterium gas at 10 psig for 1 hr. The mixture was filtered, the solvent was evaporated at reduced pressure, and methyl *threo*-hydrocinnamate-1,2-*d*$_2$ was distilled, bp 80–82° (2 mm), homogeneous by glpc (10% silicone oil, 140°). Deuterium analysis[15] showed 14.93 atom % excess deuterium, or 1.79 deuterium atoms/molecule. Reduction of the ester with $LiAlD_4$ and $LiAlH_4$ afforded the *d*$_4$- and *d*$_2$-alcohol, respectively.

A 1:1 mixture of *erythro*:*threo*-3-phenylpropanol-1,1,2,3-*d*$_4$ was prepared[16] by reduction of methyl cinnamate in ether with $LiAlD_4$.

***erythro*-3-Phenylpropanol-1,2-*d*$_2$.** A solution of 40 g (0.30 mole) of 3-phenylpropanal, 94 g (1.0 mole) of isopropenyl acetate, and 3 g of *p*-toluenesulfonic acid was heated under reflux for 22 hr. The cooled solution was diluted with 200 ml of ether, extracted with 100 ml of 10% aqueous potassium hydroxide, two 100-ml portions of 10% aqueous potassium carbonate, and finally with saturated bicarbonate solution. The dried (K_2CO_3) ether extracts were concentrated and flash distilled at 0.5 mm, bp 84–100° (0.5 mm). Nmr examination indicated a 2:1 mixture of enol acetate–aldehyde. Fractionation through a concentric tube column afforded a cut of bp 87–89° (1.8 mm), 10.5 g, whose nmr spectrum indicated a 17:1 mixture of *cis*-:*trans*-1-acetoxy-3-phenylpropene, $n^{20.5}\text{D}$ 1.5153. The nmr spectrum (CCl_4) was consistent with the assigned structure and stereochemistry, resonances appearing (Hz from internal TMS) at 125 (s,3,$-O_2CCH_3$), 210 (d, 2, $J = 8 \sim 1$ Hz, PhCH_2–), 303 (q, 1, $J = 8$, 8 Hz, *CH*=CHOAc), and 435 (m, 6, C_6H_5 and CH=*CH*OAc).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 75.17; H, 7.02.

A solution of 5.1 g (29 mmoles) of the above enol acetate was reduced in 150 ml of 2:1 cyclohexane–ethyl acetate with 0.065 g (0.29 mmole) of platinum oxide at 20-psig deuterium pressure. After uptake of gas had ceased (*ca.* 6 hr) the mixture was filtered and solvent was evaporated. The residue was crudely distilled at 1 mm (deuterium analysis, 1.55 deuteriums/molecule) and the distillate saponified by heating under reflux its solution in 60 ml of 10% ethanolic potassium hydroxide for 4 hr. The cooled solution was diluted with water, acidified, and extracted with ether. The dried ($MgSO_4$) ether extracts were concentrated and the residue was distilled, bp 69–70° (1 mm), 2.0 g. Deuterium analysis showed 13.22 atom % excess deuterium, or 1.60 deuteriums/molecule.

Acknowledgment. This work was supported entirely by grants from the National Science Foundation (GP-5061) and National Institute of Health (GM12113).

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[15] Mr. J. Nemeth, Urbana, Ill.

[16] E. I. Snyder, *J. Org. Chem.*, **32**, 3531 (1968).

Organic Quantum Chemistry. XXI.[1,2] The Structure and Spectrum of Cyclooctadecanonaene ([18]Annulene)[3]

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Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received June 20, 1968*

Abstract: An SCF modification of a previously described version of the semiempirical ASMO–CI method of Pariser and Parr has been applied to the calculation of the π-electronic transitions of a number of unsaturated hydrocarbons. This method generally predicts the electronic transitions to within 0.3 eV of the observed values. This method has been applied to various conceivable structures for the title compound and suggests that the structure best reconciled with the observed spectrum is one having alternating long and short bonds. Energy calculations, which include the compression energy of the σ system and van der Waals' interactions, also indicate that this structure is the favored one. The structure observed in the crystalline state is demonstrated to be both incompatible with the observed spectrum and energetically unfavorable, and it is concluded that it differs markedly from the structure in the gas phase. The potential curves for bond-length changes for the ground and excited states are discussed.

The compound [18]annulene (I) is one of a series of macrocyclic polyenes synthesized by Sondheimer[6] and is an important example of the compounds utilized to test the generality of Hueckel's rule,[7] that $(4n + 2)\ \pi$ electrons will yield an aromatic system. The title compound ($n = 4$) is perhaps the most well studied of this series, but is still not fully understood. It was originally predicted that the molecule would be metastable[8] at best, by virtue of the steric crowding the inner hydrogens. Hence, its very existence as a relatively stable compound poses a challenge to our understanding of the factors affecting its stability.

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[1] Paper XX: N. L. Allinger and J. C. Tai, *Theoret. Chim. Acta*, **2**, 29 (1969).

[2] This research was supported in part by Grant GP 6763, from the National Science Foundation.

[3] Abstracted in part from the Ph.D. Thesis of F. A. Van-Catledge, submitted to Wayne State University, November 1967.

[4] National Aeronautics and Space Administration Predoctoral Trainee, 1964–1967.

[5] Author to whom correspondence concerning this paper should be directed.

[6] F. Sondheimer, R. Wolovsky, and Y. Amiel, *J. Am. Chem. Soc.*, **84**, 274 (1962); and the references cited therein.

[7] E. Hueckel, *Z. Physik*, **70**, 204 (1931); **76**, 628 (1932); "Grundzuge der Theorie ungesattigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938.

[8] K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952).