Table I. Yields of Products from Reaction of Dibutylmercury in Carbon Tetrachloride[a]

Run	Hg, %[c]	BuHgCl, %[c]	TCP,[b] %[c]	BuCl, %[c]	$CHCl_3$, %[c]	Temp, °C	Conditions
1	63	25	52	51	64	100	*d*
2	63	24	54	53	64	100	*e*
3	65	25	49	54	69	100	*e*
4	2	0	0	0	0	100	*f*
5	69	13	12			77	*g*
6	73	16	53			77	*d*

[a] $[Bu_2Hg] = 0.45\ M$, [benzoyl peroxide] $= 0.056\ M$. [b] TCP = 1,1,1,3-tetrachloropentane. [c] Mol %. [d] Ampoule sealed in air. [e] Ampoule degassed. [f] No peroxide. [g] Allowing removal of the gases by fractionation.

significant that 1-chlorobutane is produced in large amounts, whereas previous workers made no mention of this product.

Consideration of the major products solely allows formulation of a tentative chain mechanism (eq 3–9).

$$\text{peroxide} \longrightarrow C_6H_5\cdot \tag{3}$$

$$C_6H_5\cdot + CCl_4 \longrightarrow C_6H_5Cl + \cdot CCl_3 \tag{4}$$

$$\cdot CCl_3 + R_2Hg \longrightarrow \text{olefin} + RHg\cdot + CHCl_3 \tag{5}$$

$$RHg\cdot + CCl_4 \longrightarrow RHgCl + \cdot CCl_3 \tag{6}$$

$$RHg\cdot \longrightarrow R\cdot + Hg \tag{7}$$

$$R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3 \tag{8}$$

$$2\cdot CCl_3 \longrightarrow C_2Cl_6 \tag{9}$$

This sequence is consistent with the products in Table I, and, as expected, small amounts of chlorobenzene and hexachloroethane were identified by glpc.

In view of the weak bond (<6 kcal) in R–Hg·,[6] a large yield of mercury is expected from RHg·, and considerable quantities of mercury were recovered. However, by the same reasoning the yield of RHgCl should be negligible. The proposed mechanism requires that the lifetime of RHg· is sufficiently long for chlorine abstraction to occur. Since the bond-energy measurements were carried out in the gas phase, the unexpected stability of RHg· in solution likely arises from complexation of RHg· with Lewis bases.

The 1-butene produced could not have resulted from disproportionation of butyl radicals since no butane is formed, nor is it likely that another process which is second order in radicals, such as disproportionation between butyl and trichloromethyl radicals, is occurring. Also, on the basis of previous studies on the reaction of radicals with mercurials,[7] phenyl radicals prefer to attack mercury. In this light the reaction of eq 5, a free-radical elimination, with trichloromethyl radicals as the chain-carrying species, is postulated to explain olefin production. Although a similar radical elimination has been reported with phenyl radicals and *t*-butyl sulfide to give isobutylene,[8] the reaction of eq 5 represents a novel reaction of radicals with dialkylmercurials. Furthermore it is very likely that this elimination is a concerted process because otherwise there is no reason to expect any special reactivity of the hydrogens β to mercury. This concerted process may involve either the loss of an alkylmercury radical or the formation of a bridged mercury radical. The bridged species could be similar to that suggested by Thaler[9] to account for the enhanced reactivity of the β hydrogens of alkyl bromides toward Br·. Further study of the generality, stereochemistry, and mechanism of this reaction is in progress.

Attempts were made to duplicate the reactions reported by Nesmeyanov, *et al.*, with butylethylmercury, butylcyclohexylmercury, and benzylcyclohexylmercury. In no case could more than a trace of the reported trichloride be detected, but instead products arising from olefins were found. However, the peroxide-induced decomposition of diphenylmercury in carbon tetrachloride under the same conditions as run 1 of Table I did yield phenylmercuric chloride (31%) and α,α,α-trichlorotoluene (25%), as previously reported by Borisov.[10]

We conclude that, although diarylmercurials are cleaved by trichloromethyl radicals to produce arylmercuric chloride and a trichloromethylaryl compound as originally reported,[1,10] dialkylmercurials are not cleaved according to eq 1 but undergo a radical β-elimination reaction (eq 5).

Acknowledgment. This work was supported by the National Science Foundation under Grant GP-6350X.

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[6] B. G. Gowenlock, J. C. Polyani, and E. Warhurst, *Proc. Roy. Soc.* (London), **A219**, 270 (1963).

[7] F. R. Jensen, J. E. Rodgers, and H. E. Guard, submitted for publication.

[8] J. A. Kampmeir, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *J. Am. Chem. Soc.*, 88, 1257 (1966).

[9] W. Thaler, *ibid.*, 85, 2607 (1963).

[10] A. E. Borisov, *Izv. Akad. Nauk SSR, Otd. Khim. Nauk*, 524 (1951).

[11] National Institutes of Health Predoctoral Fellow.

Frederick R. Jensen, Harold E. Guard[11]
Department of Chemistry, University of California
Berkeley, California 94720

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The Nuclear Magnetic Resonance Chemical Shift Method of Calculating Conformational Preferences in Cyclohexyl Derivatives

Sir:

Recently much work has appeared in which the conformational preferences, *A* values,[1] of a number of substituents have been calculated using the method of Eliel and coworkers which assumes that the chemical shifts of the axial and equatorial methine proton peaks of a cyclohexyl derivative are identical with those of the corresponding peaks of the 4-*t*-butylcyclohexyl derivative at room temperature.[2] In fact, in a recent review of the subject half of the *A* values tabulated for the cyclohexyl halides had been calculated by this procedure, and those obtained by this method were considered by the author of the article to be the best values.[3] Although, many *A* values have been determined by this method, no con-

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[1] S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, 77, 5562 (1955).

[2] (a) E. L. Eliel, *Chem. Ind.* (London), 568 (1959); (b) E. L. Eliel and R. J. L. Martin, *J. Am. Chem. Soc.*, **90**, 682 (1968); (c) E. L. Eliel and R. J. L. Martin, *ibid.*, **90**, 689 (1968); (d) J. Reisse, J. C. Celotti, and G. Chiurdoglu, *Tetrahedron Letters*, 397 (1965).

[3] J. A. Hirsch, "Topics in Stereochemistry," Interscience Publishers, Inc., New York, N. Y., 1967, p 119.

Table I. The Effect of Temperature on the Chemical Shift of the Methine Resonance in Cyclohexyl and 4-*t*-Butylcyclohexyl Derivatives[a]

		Cyclohexyl			4-*t*-Butylcyclohexyl	
X	Temp, °C	ν_{eq},[b] Hz	ν_{ax},[b] Hz	Temp, °C	ν_{eq},[b] Hz	ν_{ax},[b] Hz
Cl	+22	387.1		+22	432.7	363.3
				−47	434.2	364.2
	−83	440.0	369.4	−82	435.2	364.9
	−90	440.1	369.6	−90	435.7	365.4
	−98	440.6	369.8	−97	435.9	365.5
Br	+24	406.2		+24	452.9	380.4
	−47	397.6		−49	454.2	380.9
	−84	459.0	387.2	−84	455.3	381.7
	−91	459.7	387.4	−92	455.7	381.9
	−102	460.0	387.8	−100	456.0	382.1
OAc	+24	459.4		+24	486.3	446.5
	+23	459.2		+23	486.2	446.4
				−47	482.3	442.8
	−85	481.8	442.6	−82	479.6	440.1
	−90	481.6	442.0	−91	478.8	439.3
	−106	480.4	440.7	−106	477.6	437.9
$OOCCF_3$	+23	488.4		+24	513.2	473.9
	−86	514.2	474.7	+23	512.9	473.6
	−91	514.6	474.1	−47	512.0	473.1
	−104	513.0	473.3	−70	511.2	472.6
				−80	510.7	471.9
CN	+24	251.5		+24	279.5	221.2
	−85	287.8	233.8	−46	282.2	223.5
	−91	288.6	234.6	−84	284.1	225.5
	−102	289.2	235.2	−91	284.4	226.0

[a] 0.50 ± 0.01 *M* in CS_2 containing 15% TMS as an internal standard. [b] Measured from TMS.

clusive evidence has been presented which proves that the assumptions on which this procedure is based are correct even though these assumptions are very easy to test. The simplest test of this method's validity is to cool samples of both 4-*t*-butylcyclohexyl and cyclohexyl derivatives to below −80° and examine their nmr spectra. At this temperature the cyclohexyl ring inversion is sufficiently slow to allow precise determination of the axial and equatorial methine proton chemical shifts.

Samples were prepared (0.5 *M* in CS_2 containing 15% TMS) of the cyclohexyl and the *cis*- and *trans*-4-*t*-butylcyclohexyl derivatives. The bromo-, chloro-, acetoxy-, trifluoroacetoxy-, and cyanocyclohexyl and -4-*t*-butylcyclohexyl compounds were studied. To check for possible solvent effects, samples which contained a mixture of the cyclohexyl and 4-*t*-butylcyclohexyl derivatives were also prepared. At room temperature the chemical shifts of the methine protons were carefully measured in both the samples of the individual compounds and those containing the mixture of the 4-*t*-butylcyclohexyl and cyclohexyl derivatives. The deviation for a particular resonance was in no case larger than 0.3 Hz. It is a reasonable conclusion that any significant difference observed at low temperature between the various axial resonances or between the various equatorial resonances is not the result of a solvent effect. At low temperatures (between −80 and −105°) significant differences were observed in all cases between the axial and equatorial methine proton resonances of the cyclohexyl derivatives and those of the corresponding 4-*t*-butylcyclohexyl derivatives (Table I). The differences range from ~2.6 Hz for the axial proton of the acetoxy derivatives to ~8.5 Hz for the axial resonance of the cyano derivatives. In all cases the chemical shift (from TMS as an internal standard) was larger for the cyclohexyl derivative than for the corresponding 4-*t*-butyl compound. These very simple experiments prove conclusively that the chemical shift method of Eliel for determining *A* values is invalid. (The magnitudes of the resulting errors are indicated by the data in Table II.)

Table II. *A* Values for Cyclohexyl Derivatives[a]

	A values, kcal/mol		
Derivative	Peak area measurement, ~−83°	Method I[b] 25°	Method II[c] 25°
Br	0.49	0.55	0.35
Cl	0.53	0.57	0.39
$OOCCF_3$	0.54	0.55	0.31
OAc	0.72	0.64	0.44
CN	0.22	0.23	−0.04

[a] Concentration = 0.50 ± 0.01 *M* in CS_2 containing 15% TMS by volume. [b] In method I, the resonances of the individual axial and equatorial methine protons of the monosubstituted cyclohexane are measured below −80° and extrapolated to room temperature by assuming that the effect of temperature upon these individual resonances is the same as that on the resonance of the corresponding 4-*t*-butylcyclohexyl derivative. [c] In method II, that of Eliel and coworkers, the resonances of the individual axial and equatorial methine protons of the monosubstituted cyclohexanes at room temperature are assumed to equal those of the corresponding 4-*t*-butylcyclohexyl derivatives at this temperature.

From plots of the individual chemical shifts of the axial and equatorial resonances of these compounds as a function of temperature between −80 and −105°, it appears that the movements of the axial and equatorial peaks of the cyclohexyl derivatives parallel those of the corresponding 4-*t*-butyl derivatives within the uncertainty of the experiment. This observation indicates that, at temperatures at which the ring inversion is rapid on the nmr time scale, good estimates of the nonmeasurable axial and equatorial resonances of monosubstituted cyclohexanes can be obtained by assuming that the variations with temperature of the chemical shifts of the individual types of resonances in the cyclohexyl and 4-*t*-butylcyclohexyl derivatives are the same. Thus the chemical shift of the individual resonances of the cyclohexyl derivative at room temperature can be approximated by correcting the observed individual low-temperature resonances in the monosubstituted cyclohexanes by the change observed between low temperature and room temperature for the corresponding resonances of the 4-*t*-butylcyclohexyl compounds. *A* values calculated from these corrected chemical shifts are tabulated in Table II. The *A* values were also measured by the peak area measurement method[4] at about −80°. For comparison, the values determined by the method of Eliel and coworkers are also included. They differ considerably from those obtained by the method outlined herein.

Acknowledgment. This research was supported by Public Health Service Grant GN-15373 and National Science Foundation Grant GP-6350X.

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Frederick R. Jensen, Barbara Hardin Beck
Department of Chemistry, University of California
Berkeley, California 94720
Received May 1, 1968

The Crystal Structure of *o*-Di-*t*-butylquinoxaline

Sir:

Continued interest in the synthesis and the chemical and physical properties of *o*-di-*t*-butyl aromatic systems has made it important to know the detailed molecular structure of at least some representative compounds. Recently Arnett and coworkers[1] reported that C. H. Stam (Amsterdam) had carried out an X-ray analysis of 1,2,4,5-tetra-*t*-butylbenzene, but no details were given.[1a]

We wish to report the results of a refined X-ray analysis of 2,3-di-*t*-butylquinoxaline (Figure 1)[2] taken at room temperature. Suitable crystals of 2,3-di-*t*-butylquinoxaline (mp 53–54°)[3] were obtained from a solution in petroleum ether (bp 60–80°). The unit cell of 2,3-di-*t*-butylquinoxaline was found to be monoclinic with $a = 10.048 \pm 0.010$ Å, $b = 9.923 \pm 0.004$ Å, $c = 29.002 \pm 0.010$ Å; $\beta = 91.76 \pm 0.01°$. The space group is $P2_1/c$ with eight molecules per unit cell, and consequently there are two independent molecules.

The 3296 reliable *hkl* intensities (out of 6500 reflections measured) were measured by an automatic Nonius diffractometer. No absorption corrections needed to be applied. The structure was solved by means of the symbolic addition method[4] and refined by anisotropic least-squares methods on a TR4 computer.[5] The hydrogen atoms were located from a difference map and included in the refinement with fixed parameters, and this resulted in a final *R* value of 0.075.

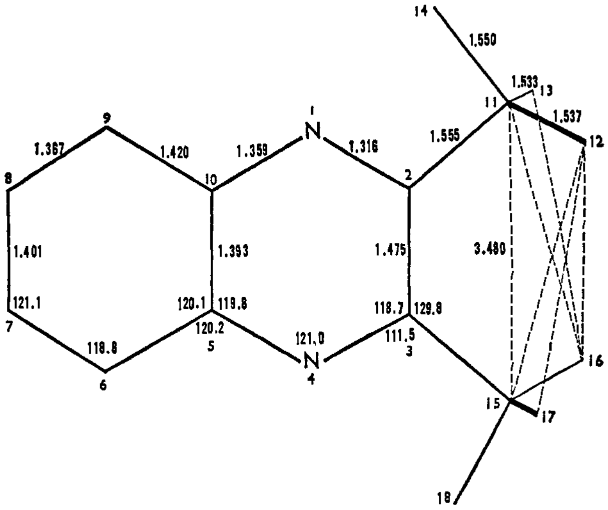

Figure 1. The bond lengths and angles of the average 2,3-di-*t*-butylquinoxaline molecule as projected onto the average plane of atoms 1–10.

The values of chemically equivalent bonds and angles in the two molecules are not significantly different; average values are given in Figure 1. The six distances, indicated in Figure 1, between the *t*-butyl groups fixed at one ring range from 3.33 to 3.50 Å.

The estimated standard deviations following from the least-squares refinement are 0.006–0.010 Å in the bond lengths and 0.4–0.6° for the bond angles. Meanwhile a refinement of data collected at −150° has been undertaken.[6]

This appears to be the first experimental evidence about bond lengths and angles in an *o*-di-*t*-butyl compound.

The distances between all of the methyl groups of the two *t*-butyl groups are such that we can speak of a fit between these groups as in a gear. The angles at the bonds C_{11}–C_{12} and C_{15}–C_{16} deviate from the normal value of 109.5° such as to increase the $C_{12} \cdots C_{16}$ distance; observed values are 113–116° for angles of type C_{12}–C_{11}–C_2, 112–114° for C_{12}–C_{11}–C_{13}, and 104–106° for C_{12}–C_{11}–C_{14}.

In both types of molecules carbons 11, 2, 3, and 15 are in one plane. Significant is the 129.8° external C_2–C_3–C_{15} angle. This is a 10° deviation from the similar angle in 2,3,5,6-tetramethylpyrazine (see Figure 2).

A slight but perhaps significant amount of bond stretching is noticeable between ring carbon atoms 2 and 3. This bond length is 1.475 Å compared to 1.434 Å in the pyrazine ring.[7] The C_2–C_{11} bond appears to be stretched also, 1.555 Å in the quinoxaline as compared to 1.505 Å in the pyrazine (see Figure 2). Although one molecule is completely planar, the other one is nearly, but not completely, so. The latter molecule shows a

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(1) E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *J. Am. Chem. Soc.*, 89, 5389 (1967). Arnett's paper contains an up-to-date bibliography of papers pertaining to *o*-di-*t*-butylbenzenes but excludes heteroaromatic analogs.

(1a) NOTE ADDED IN PROOF. See, however, A. van Bruijnsvoort, L. Eilermann, H. van der Meer, and C. H. Stam, *Tetrahedron Letters*, 2527 (1968).

(2) The numbering of the atoms in Figure 1 is completely arbitrary and has no relation to the normal numbering in quinoxalines.

(3) Ae. de Groot and H. Wynberg, *J. Org. Chem.*, 31, 3954 (1966).

(4) Performed in the Naval Research Laboratory, Washington, D. C., with computer programs written by Dr. S. Brenner; see J. Karle and I. L. Karle, *Acta Cryst.*, 21, 849 (1966).

(5) D. W. J. Cruickshank, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon Press, Ltd., London, 1961.

(6) The results and the comparison with this room-temperature refinement will be published in *Acta Crystallographica*.

(7) D. T. Cromer, *J. Phys. Chem.*, 61, 254 (1957).