Anal. Calcd. for $C_{11}H_{19}NO_5{\cdot}HCl$: C, 46.89; H, 7.16; Cl, 12.59. Found: C, 47.20; H, 7.18; Cl, 12.56.

3-Benzyl-2,4-dioxo-7-methoxy-9-methyl-3,9-diazabicyclo[3.3.1]-nonane.—A stirred mixture of 125.9 g. (0.514 mole) of dimethyl 4-methoxy-1-methylpiperidine-2,6-dicarboxylate and 138.0 g. (1.29 moles) of benzylamine was heated to reflux (168°). Soon after refluxing had begun, the temperature began to fall, and was at 148° after half an hour. It was heated for 48 hr. The apparatus was then changed for distillation, and the mixture heated at 200° for 0.5 hr., again changed to refluxing, and heated at 140° for 5 hr., followed by heating at 200° for an hour. The hot material was transferred to a beaker; upon cooling, it assumed the appearance of cold honey. It was beaten twice each time with 200 cc. of saturated salt solution, and the organic layer was taken up in 1 l. of benzene. The solvent was removed from the dried solution, leaving 202.5 g. of an orange sirup which was extracted thrice with heptane, each time using 700 ml. of the solvent. The residual material (91.2 g.) solidified on cooling; this was the diamide type VII. Concentration of the liquors gave the impure imide as a viscous residue which solidified incompletely on standing. It was collected at the pump, and the oil expressed as completely as possible before it was dried on porous porcelain to yield *ca.* 74 g. of waxy solid. The pure compound (45.2 g., 30.2%) was obtained following several crystallizations from pentane, whence it separated as a cryptocrystalline mass, m.p. 66–68°.

Anal. Calcd. for $C_{16}H_{20}N_2O_3$: N,[10] 4.85. Found: N,[10] 4.86.

The hydrochloride of 3-benzyl-2,4-dioxo-7-methoxy-9-methyl-3,9-diazabicyclo[3.3.1]nonane could be obtained from the oily or waxy impure base. It was formed in, and crystallized from, propanol, from which it crystallized as fine needles, m.p. 172.5–173°, with intumescence.

Anal. Calcd. for $C_{16}H_{20}N_2O_3{\cdot}HCl$: N, 8.63; N,[10] 4.32; Cl, 10.92. Found: N, 8.33; N, (basic[10]), 4.46; Cl, 11.09.

The crude residue of 2,6-bis(benzylcarbamyl)-4-methoxy-1-methylpiperidine, 91.2 g., was leached in the hot with cyclohexane and crystallized from ethanol. A rather amorphous product resulted, m.p. 103–105°.

Anal. Calcd. for $C_{23}H_{29}N_3O_3$: N, 10.63; N (basic[10]), 3.54. Found: N, 10.38; N (basic[10]), 3.51.

3-Benzyl-7-methoxy-9-methyl-3,9-diazabicyclo[3.3.1]nonane was prepared by lithium aluminum hydride reduction of the 2,4-dioxo compound. The yield of crude golden base was 93.5%. A dihydrogen citrate (m.p. *ca.* 125°, with intumescence) was formed in ether solution, although it became sticky upon attempts to purify it. The base was distilled and an 88% recovery of a pale yellow oil was obtained; b.p. 127–129° (0.02 mm.), $n^{25}{}_D$ 1.5350. Values for carbon and hydrogen were consistently low in an erratic pattern.

Anal. Calcd. for $C_{16}H_{24}N_2O$: N, 10.77; O, 6.15. Found: N, 10.59; O, 6.47.

Acknowledgment.—The friendly support and encouragement by Dr. C. M. Suter and (the late) Dr. J. S. Buck materially aided this investigation.

Structural Determination of *cis*- and *trans*-1,3-Dibromocyclohexane[1]

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Received January 7, 1963

The structures of the *cis*- and *trans*-1,3 and 1,4-dibromocyclohexanes have heretofore been difficult to resolve because of the reaction of the corresponding diols with either hydrobromic acid or phosphorus tribromide results in a mixture of both *cis*- and *trans*-1,3 and 1,4-dibromocyclohexanes. All four isomers have been isolated and identified. Identification of the *cis*- and *trans*-1,4-dibromocyclohexanes has been achieved by dipole moment measurements. As both *cis*- and *trans*-1,3-dibromocyclohexanes have the same dipole moment, assignment of structure was made by variable temperature n.m.r. analysis. Thus the bromines of *cis*-1,3-dibromocyclohexane exist entirely in the diequatorial conformation and this isomer exhibits no significant change in its n.m.r. spectrum from −72° to 200°. The *trans*-1,3-dibromocyclohexane, which shows no change in its n.m.r. spectrum on heating, does exhibit a change in spectrum at −33°. At this temperature the chair–chair interconversion is sufficiently slow so that the C-2 hydrogens are no longer equivalent and the A_2X_2 multiplet is not exhibited.

The 1,3-dibromocyclohexanes have been described as a solid with a m.p. of 48–49°[3]; specifically, the 48–49° isomer has been assigned the *trans*-1,3 structure[4a] and the *cis*-1,3 structure.[4b] The *cis*-1,3 structure also has been assigned to a 112° isomer.[5a,b] The correct structures for the 1,4-dibromocyclohexanes (*trans*-1,4, m.p. 112°; *cis*-1,4, m.p. 48°) has been summarized by Cornubert, Rio, and Senechal[6a] and by Grob and Baumann.[6b] The individual 1,4-dibromocyclohexanes at times have been correctly identified,[4a,5a,6a,b,7] but the 1,3-dibromocyclohexanes have not been correctly characterized.

We have treated 1,3- and 1,4-cyclohexanediols with both aqueous hydrobromic acid and with phosphorus tribromide and have analyzed for the 1,3- and 1,4-dibromides by vapor phase chromatography. In order to ascertain the positional integrity of the diols, known derivatives of each of the diols were synthesized. Thus we could always be sure that the 1,3-diol was uncontaminated with any 1,4-diol and *vice versa*.

A purchased sample of 1,4-cyclohexanediol was identical to the diol prepared from reduction of 1,4-cyclohexanedione. The *cis*- and *trans*-ditosylates of 1,4-cyclohexanediol were prepared, separated, and the melting points compared with the known ditosylates.[8] This series of reactions confirmed the positional integrity of the 1,4-diol. The 1,4-diacetates also were made,[8,9] and the *cis*- and *trans*-isomers were detected by v.p.c. both before and after isolation. Similarly the 1,3-diacetates were synthesized[10] and the *cis*- and *trans*-isomers separated by v.p.c. The v.p.c. retention times of the *cis*- and *trans*-1,4 diacetates differed from those of the 1,3-diacetates. Although one of the 1,3-diacetates differed only slightly in retention time from *cis*-1,4-cyclohexanediol diacetate, these two compounds were shown to be different isomers by comparison of

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[1] Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 5, 1963.

[2] Analytical Research Division, Esso Research and Engineering Co.

[3] L. Palfray and B. Rothstein, *Compt. rend.*, **189**, 701 (1929).

[4] (a) N. D. Zelinsky and K. A. Kozeschkow, *Ber.*, **60B**, 1102 (1927); (b) J. G. Gudmundsen and O. Hassel, *Z. Physik. Chem.*, **B40**, 326 (1938).

[5] (a) H. Lindermann and H Baumann *Ann.*, **477**, 78 (1929); (b) M. S. Kharasch, S. Sallo, and W. Nudenberg, *J. Org. Chem.*, **21**, 129 (1956).

[6] (a) R. Cornubert, A. Rio, and P. Senechal, *Bull. soc. chim. France.* 46 (1955); (b) C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955),

[7] S. Furberg and O. Hassel, *Acta Chem. Scand.*, **6**, 1300 (1952).

[8] L. N. Owen and P. A. Robins, *J. Chem. Soc.*, 320 (1949).

[9] T. D. Perrine and W. C. White, *J. Am. Chem. Soc.*, **69**, 1542 (1947).

[10] W. Rigby, *J. Chem. Soc.*, 1586 (1949).

their infrared spectra after isolation by v.p.c. The positional integrity of the 1,3- and 1,4-diols was thus confirmed.

The reaction of hydrobromic acid with either 1,3- or 1,4-cyclohexanediol (both 1,3- and 1,4-diols are almost equal mixtures of *cis* and *trans* isomers), leads to an almost random distribution of 1,3- and 1,4-dibromocyclohexanes. As shown in Table I, the main difference between the 1,3- and 1,4-diol in product distribution is a marked change in the quantity of *cis*-1,4-dibromocyclohexane and *trans*-1,3-dibromocyclohexane.

TABLE I

REACTION PRODUCTS FROM 1,3- AND 1,4-CYCLOHEXANEDIOLS AND HYDROBROMIC ACID

Dibromocyclohexane isomer	Yield, % From 1,3-diol	From 1,4-diol
trans-1,3	32.6	20.6
trans-1,4	30.9	23.2
cis-1,3	21.9	25.6
cis-1,4	14.6	31.6

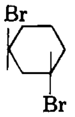
The reaction of the diols with phosphorus tribromide leads to less rearrangement, but, as shown in Table II, one cannot be assured of replacing a hydroxyl group by a bromine atom without rearrangement.

TABLE II

REACTION PRODUCTS FROM 1,3- AND 1,4-CYCLOHEXANEDIOLS AND PHOSPHORUS TRIBROMIDE

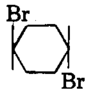
Dibromocyclohexane isomer	Yield, % From 1,3-diol	From 1,4-diol
trans-1,3	33.7	24.5
trans-1,4	22.8	30.4
cis-1,3	29.6	7.5
cis-1,4	13.9	37.6

Since the 1,3-dibromides could not be obtained without contamination by the 1,4-dibromides and *vice versa*, separation of the four isomers was accomplished by a combination of both column chromatography and preparative gas chromatography. Analysis for the various isomers was accomplished by v.p.c. using an ethylene glycol succinate substrate. On this substrate, the order of increasing retention time was *trans*-1,3 (**1**), *trans*-1,4 (**2**), *cis*-1,3 (**3**), and finally *cis*-1,4 (**4**).



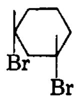
liquid

1



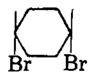
m.p. 111.5-112°

2



liquid

3



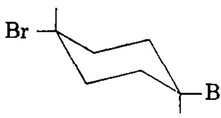
m.p. 48°

4

The individual isolated isomers all gave the correct carbon, hydrogen, and bromine analyses and molecular weight for $C_6H_{10}Br_2$, substantiating the proposed cyclic structure. In order to obtain more information regarding the structure of the dibromocyclohexanes, dipole moments of all four dibromides were determined. Molar polarization at infinite dilution ($P_{2\infty}$) was calculated by the method of Hedestrand[11] and the dipole moments calculated from the Debye equation.

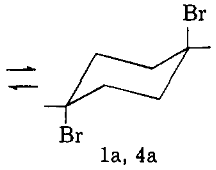
$$\mu = 0.01281 \times 10^{-18}[(P_{2\infty} - R_D)T]^{1/2}$$

The molar refraction of the solute, R_D, was calculated from group refractions. This assumption is not unreasonable since the calculated R_D (from group refractions) was 43.24 whereas the calculated R_D (from density and index of refraction) of the combined four isomers was 43.37. The assumed R_D value is reasonably close to results obtained by Bender, Flowers, and Goering.[12] From their densities and indices of refraction[12] we calculated the R_D value for *cis*-1,2-dibromocyclohexane to be 42.87, for *trans*-1,2-dibromocyclohexane it was 43.26, and for 1,1-dibromocyclohexane, R_D was 43.52. The theoretical calculation of dipole moments was based on a technique used by Wilcox[13] and on a cyclohexane model first used by Corey and Sneen[14]; the details for this method are more elaborately described in the Experimental section of the paper. Table III gives the calculated dipole moments for the possible conformations of the 1,3- and 1,4-dibromides as well as the observed dipole moments for all the isomeric dibromocyclohexanes. A bond moment of



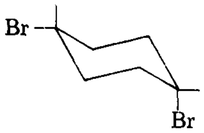
1e, 4e

5



1a, 4a

6

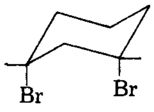


1e, 4a≡1a, 4e

7

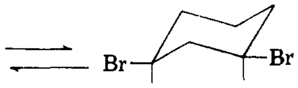
1e, 3a≡1a, 3e

8



1a, 3a

9



1e, 3e

10

TABLE III

CALCULATED AND OBSERVED DIPOLE MOMENTS OF DIBROMOCYCLOHEXANES

Dibromo-cyclohexane	Position and orientation of bromines	$\mu_{\text{calcd}} \times 10^{18}$	$\mu_{\text{obsd}} \times 10^{18}$
trans-1,4	1e, 4e(**5**)	0	0.55[a]
trans-1,4	1a, 4a(**6**)	0	0.55[a]
cis-1,4	1e, 4a(**7**)	3.11	2.92[b]
trans-1,3	1e, 3a(**8**)	2.21	2.17
cis-1,3	1a, 3a(**9**)	3.82	2.19
cis-1,3	1e, 3e(**10**)	2.20	2.19
cis-1,2	1e, 2a		3.06[c]
trans-1,2	1e, 2e ⇌ 1a, 2a		1.74[c,d]
1,1-Dibromo-cyclo-hexane	1e, 1a		2.44[c]

[a] *Cf.* ref. 15, 0.56 D., and ref. 16, 0.4 D., both in carbon tetrachloride. [b] *Cf.* ref. 15, 2.89 in carbon tetrachloride and 2.93 in benzene [c] *Cf.* ref. 12, in carbon tetrachloride. [d] *Cf.* ref. 17, in heptane.

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(11) C. Hedestrand, *Z. Physik. Chem.*, **B2**, 428 (1929).

(12) P. Bender, D. L. Flowers, and H. L. Goering, *J. Am. Chem. Soc.*, **77**, 3463 (1955).

(13) C. F. Wilcox, Jr., *ibid.*, **82**, 414 (1960).

(14) E. J. Corey and R. A. Sneen, *ibid.*, **77**, 2505 (1955).

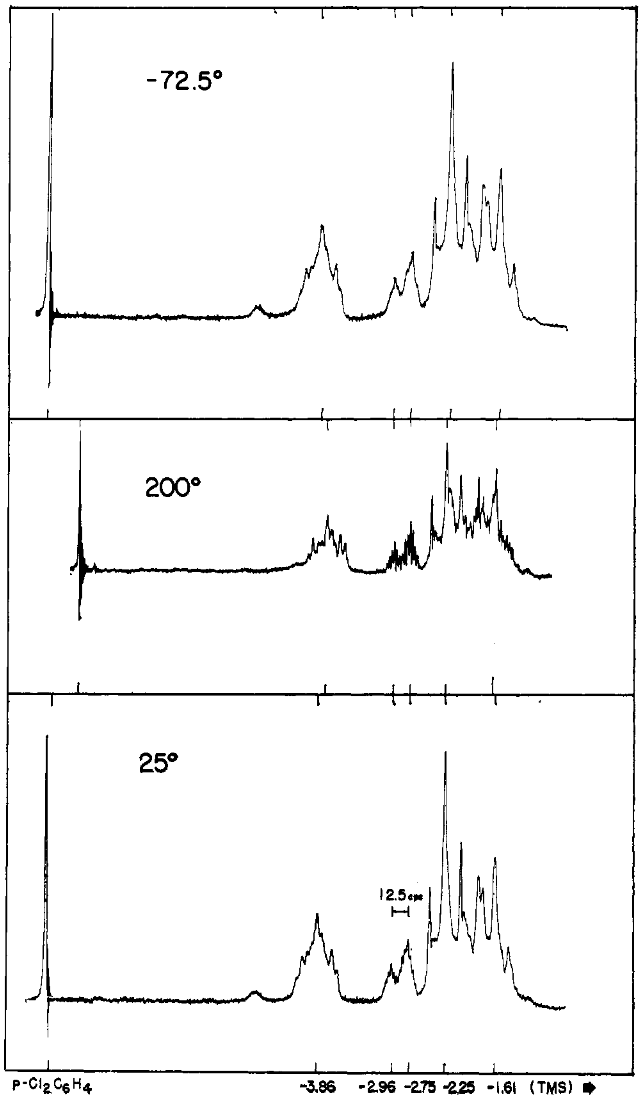

Fig. 1.—N.m.r. spectra of *cis*-1,3-dibromocyclohexane; at 200° no solvent, at 25° and below solvent was carbon disulfide.

1.91 D. was used as the apparent C–Br bond moment; this is based on the results of dipole moment calculations for the 1,2-dibromocyclohexane isomers.[12]

The observed dipole moment of the *trans*-1,4 isomer is not without precedence since a value of 0.56 D. has also been observed by Kwestroo, Meijer, and Havinga.[15] Although it has been reported by Kozima and Yoshino[16] that the *trans*-1,4-dibromocyclohexane has zero dipole moment, their $P_{2\infty}$ and R_D values lead to a dipole moment of 0.4 D. The use of heptane as solvent should introduce no difficulty since the dipole moment of the *trans*-1,2-isomer is the same in heptane[17] as it is in carbon tetrachloride.[12]

The assignment of *cis*-1,4-dibromocyclohexane to that isomer having a dipole moment of 2.92 D. and a melting point of 48° is unequivocal. The only other compound having a dipole moment near the 3.10 D. theoretical value is *cis*-1,2-dibromocyclohexane, a liquid at room temperature. The assignment of the *trans*-1,4-dibromocyclohexane structure to the isomer having a melting point of 112° is also unequivocal since none of the other dibromides has as low a dipole moment as this isomer. The compound, 1,1-dibromocyclohexane, is ruled out by the observed n.m.r. spectra of the dibromides. The *trans*-1,2-structure is ruled out by both the observed dipole moment and by the fact that an authentic sample of *trans*-1,2-dibromocyclohexane has a far shorter retention time in v.p.c. analysis than any of the 1,3- or 1,4-dibromides. There is no doubt that the 1,3-dibromocyclohexanes were correctly labeled; however, by dipole moment there is no way to distinguish between the *trans*-1,3-dibromocyclohexane which is equatorial–axial and the *cis*-1,3-dibromocyclohexane which is diequatorial. The calculated dipole moments for the two conformations of the *cis*-1,3-dibromocyclohexane were 3.82 D. for the diaxial and 2.21 D. for the diequatorial. The observed dipole moments for the *cis*- and *trans*-1,3 isomers were 2.19 and 2.17 D., respectively. Therefore, the most probable conformation of the *cis*-1,3-dibromocyclohexane is diequatorial. Further calculations show that the bromine–bromine distance in the 1,3-diaxial position is 2.53 Å. Since the van der Waals distance for bromine is 3.90 Å., the steric strains involved virtually rule out the 1,3-diaxial conformation. On this basis, the von Auwers-Skita rule that fully equatorial conformations have lower densities and refractive indices than isomers with conformations partially axial[18] leads to the correct assignment of structure. Final proof of the 1,3-conformations was established by n.m.r. N.m.r. spectra of the 1,3-dibromocyclohexanes differ markedly from each other at room temperature and exhibit some of the general features of the spectra of *cis*- and *trans*-1,3-cyclohexanediols published recently.[19] Furthermore, as shown in Fig. 1 and 2, the spectrum of one of the 1,3-dibromocyclohexane isomers (*cis*) is essentially invariant with temperature from −72.5° to +200°, while the spectrum of the other (*trans*) undergoes an abrupt change in character at −33°. We associate this change in spectral character at low temperatures with a decrease in rate of chair–chair interconversion of the *trans* isomer.

Since the diaxial conformer of the *cis* isomer is energetically disfavored by van der Waals forces, the diequatorial conformer predominates at all temperatures. The diequatorial *cis*-1,3-dibromocyclohexane, therefore, can be expected to have the time–average properties of a rigid molecule[20] essentially unaffected by temperature. In contrast, the character of the spectrum of the *trans* isomer, involving the rate of interconversion of equal energy (superimposable) conformers, can be expected to be temperature dependent. Cyclohexane, for example, inverts rapidly at ambient temperatures, and at −70° the rate becomes slow relative to the time scale involved in the method of observation.[21] Other cyclic structures having equal-energy conformers have been shown to behave analogously[22] on cooling. Activation energies were generally in the range 9–19 kcal./mole.

Resonance assignments to the protons of the *cis*- and *trans*-dibromocyclohexanes are largely obvious on the basis of chemical shifts. The low-field multiplets (*cis*,

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[15] W. Kwestroo, F. A. Meijer, and E. Havinga, *Rec. trav. chim.*, **73**, 717 (1954).

[16] K. Kozima and T. Yoshino, *J. Am. Chem. Soc.*, **75**, 166 (1953).

[17] K. Kozima, K. Sakashita, and S. Maeda, *ibid.*, **76**, 1965 (1954).

[18] M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 21.

[19] H. Finegold and H. Kwart, *J. Org. Chem.*, **27**, 2361 (1962).

[20] J. I. Musher, *J. Chem. Phys.*, **34**, 594 (1961).

[21] F. R. Jensen, D. S. Noyce, C. S. Sederholm, and A. J. Berlin, *J. Am. Chem. Soc.*, **82**, 1256 (1960).

[22] G. Claeson, G. Androes and M. Calvin, *ibid.*, **83**, 4357 (1961).

−3.86 p.p.m.; *trans*, −4.47 p.p.m.) originate from protons on the brominated carbons 1 and 3. That this resonance appears at higher field in the case of the *cis* isomer is directionally consistent with the axial orientation[23] of both the 1 and 3 protons of the dominant conformer of this isomer. High-field areas include methylene protons on carbons 4, 5, and 6 of both isomers, and one of the C-2 protons in the case of the *cis* isomer. Absorption at −2.75 and −2.96 p.p.m. in the spectrum of the *cis* isomer represents a single proton and has the appearance of the low-field portion of an AB quartet, J_{gem} = 12.5 c.p.s. This is assigned to the equatorial C-2 proton. The corresponding high-field portion of the AB pattern (axial C-2 proton) overlaps resonances of the C-4, C-5 and C-6 protons. The difference in chemical shift, δ_{ae}, for the C-2 protons of the *cis* isomer is estimated to be at least 0.5 p.p.m.

The mid-field multiplet (−2.39 p.p.m.) of the *trans* isomer has an area corresponding to two protons and is assignable to the C-2 hydrogens on the basis of chemical shift. The triplet form of this multiplet at temperatures substantially above −33° suggests that it represents one part of an A_2X_2 pattern. The phenomenon of averaging through fast inversion would be expected to equalize chemical shifts of the two C-2 protons and simultaneously equalize the coupling constants of each to the vicinal C-1 and C-3 protons. The apparent coupling constant, 5.5 c.p.s., is equal in magnitude to the arithmetic mean of typical axial–axial (8 c.p.s.) and axial–equatorial (3 c.p.s.) coupling constants. Triplet splittings of 5.6 c.p.s. and 5.4 c.p.s. were observed for the corresponding absorption in the spectra of *trans*-1,3-cyclohexanediol and *trans*-5,5-dimethyl-1,3-cyclohexanediol by Finegold and Kwart.[19] These authors reasoned that the *trans*-1,3 diols inverted rapidly at room temperature on the basis of analogies which also involved averaging the chemical shifts of axial and equatorial methyl groups, by rapid inversion, in the spectrum of *trans*-1,1,4,4-tetramethylcyclohexyl 2,6-diacetate.

Although it has been pointed out[19,24a,b] that, with certain relationships of coupling constants, ABXY spin systems might also give triplet patterns, we conclude from the drastic effect of temperature change on the spectrum of the *trans*-1,3-dibromocyclohexane in the region of −33° and upward that indeed a significant degree of averaging by rapid inversion does take place. In parallel with the sharpening of the C-2 proton triplet with increasing temperature, the rudiments of a quintet appear in the C-1, C-3 proton multiplet. The low temperature spectrum of the *trans* isomer did not change appreciably from −33° to the freezing point of the solution (below −100°). Thus, it can be estimated that δ_{ae} of the C-2 protons is probably not greater than 0.2 p.p.m. under conditions of slow inversion.

The preference of an equatorial bromine over an axial bromine is estimated to be from −0.73 kcal./mole[25] to −0.61 kcal./mole.[26] Using a mean value of −0.67 kcal./mole, the equilibrium constant for **9** ⇌ **10** should vary from 29.4 at −73° to 9.7 at 25° to 4.2 at 200°. This would mean a decrease of the diequatorial conformer from 97 to 91 to 81%.

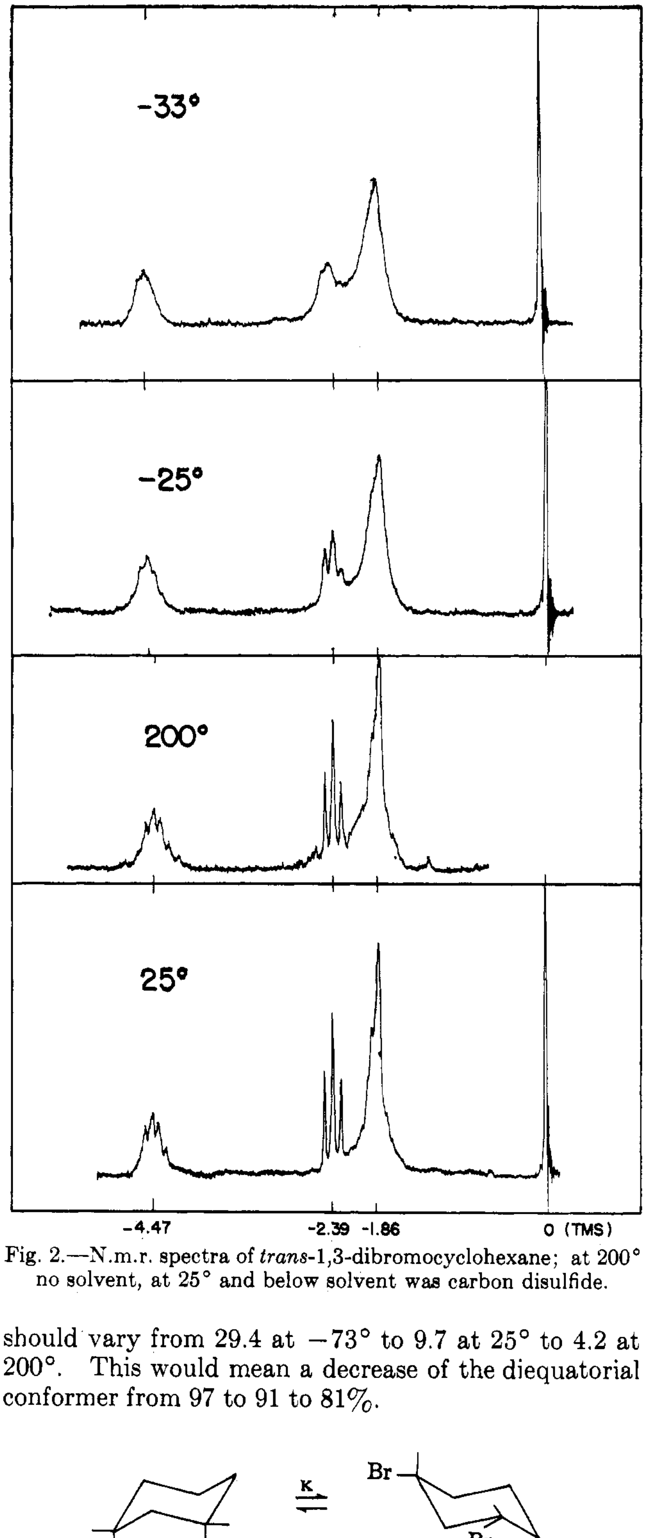
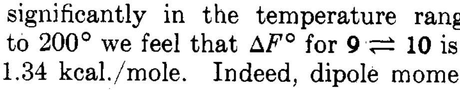


Fig. 2.—N.m.r. spectra of *trans*-1,3-dibromocyclohexane; at 200° no solvent, at 25° and below solvent was carbon disulfide.



9 **10**

If it is assumed that n.m.r. spectrum of the diaxial conformer differs noticeably from the diequatorial conformer, this per cent difference should be detectable. Since the n.m.r. of *cis*-1,3-dibromocyclohexane does not change significantly in the temperature range from −72.5° to 200° we feel that $\Delta F°$ for **9** ⇌ **10** is greater than −1.34 kcal./mole. Indeed, dipole moments and n.m.r. indicate that $\Delta F°$ for **9** ⇌ **10** is probably greater than −2.0 kcal./mole. This minimum value is not unreasonable in view of the fact that in the 1,3-diaxial

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[23] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

[24] (a) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961); (b) D. M. Grant and H. S. Gutowsky, *J. Chem. Phys.*, **34**, 699 (1961).

[25] E. L. Eliel and R. G. Haber, *J. Am. Chem. Soc.*, **81**, 1249 (1959).

[26] F. R. Jensen and L. H. Gale, *J. Org. Chem.*, **25**, 2075 (1961).

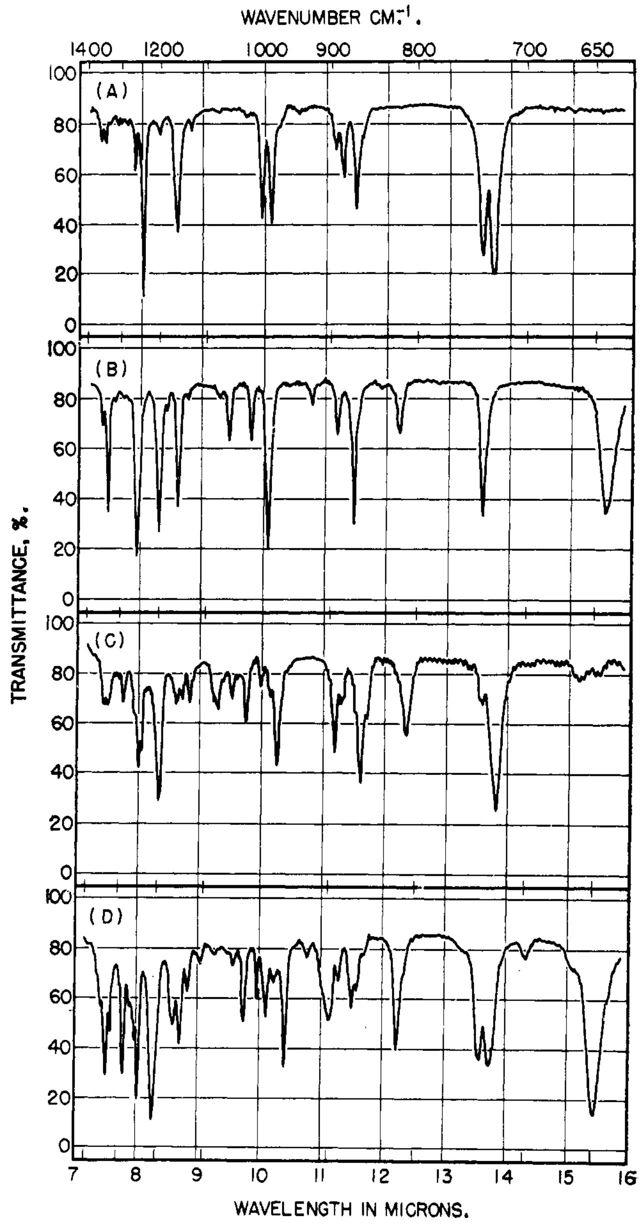

Fig. 3.—Infrared spectra of the dibromocyclohexanes; concentration, 20% in carbon disulfide. Cell thickness, 0.05 mm. (A) *trans*-1,4-Dibromocyclohexane. (B) *cis*-1,4-Dibromocyclohexane. (C) *trans*-1,3-Dibromocyclohexane. (D) *cis*-1,3-Dibromocyclohexane.

conformation the bromines would be closer than van der Waals distance for bromine to bromine.

In the reaction of 3-bromocyclohexene with aqueous hydrobromic acid, Cornubert, Rio, and Senechal[6a] have claimed the preparation of *trans*-1,3-dibromocyclohexane. Their proof of structure was in part based on the comparison of reactivity of the 1,3-dibromides with the 1,4-dibromides toward sodium iodide and sodium. In our repeat of the hydrobromic acid addition to 3-bromocyclohexene we found both the 1,3 and 1,4-dibromides along with *trans*-1,2-dibromocyclohexane. Of the total 1,3 and 1,4-dibromides the *cis*-1,3-dibromocyclohexane comprised 43% and the *trans*-1,3-dibromocyclohexane made up 23% of the total. It is significant that in the reaction of gaseous hydrogen bromide with 3-bromocyclohexene[5b] the infrared spectrum of the dibromide obtained by Kharasch, Sallo and Nudenberg corresponds quite closely to the infrared spectrum of the *cis*-1,3-dibromocyclohexane (D) of Fig. 3. Because *cis*-1,3-dibromocyclohexane has all the infrared absorption bands of the *trans*-1,3 isomer (C), the *cis*-1,4-isomer (B), and the *trans*-1,4 isomer (A), it becomes almost impossible to tell by infrared the amount of the latter three isomers in the presence of any *cis*-1,3-dibromocyclohexane. However, the purity of any future preparations of 1,3-dibromocyclohexanes should be readily established by v.p.c. data, and the infrared spectra shown in Fig. 3.

Experimental

All melting points are corrected and were taken on a Fisher-Johns melting point apparatus. Boiling points are uncorrected.

Infrared spectra of the *cis*- and *trans*-1,3- and 1,4-dibromocyclohexanes were recorded on both a Baird Model 4-55 and a Beckman IR-5 spectrophotometer. All ultraviolet analyses were determined on a Cary Model 14 spectrophotometer. Vapor phase chromatography analyses were carried out on a Perkin-Elmer Model 154-D vapor fractometer. Dipole moments were determined with the use of a Sargent oscillometer. N.m.r. spectra were recorded with Varian Associates A-60 and HR-60 spectrometers. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Molecular weights were determined by the Analytical Research Division of Esso Research and Engineering Co.

Positional Integrity of the Diols.—The reduction of 1,4-cyclohexanedione (purchased from the Aldrich Chemical Co., Milwaukee, Wis.), m.p. 79–80° (reported[27] 79.5°), to *cis*- and *trans*-1,4-cyclohexanediol was done in the usual manner with sodium borohydride. The *cis*- and *trans*-1,4-cyclohexanediol di-*p*-toluenesulfonates were prepared by the method of Owens and Robins.[8] Recrystallization from methanol gave the *trans*-1,4-ditosylate, m.p. 154–155° (Owens and Robins, m.p. 159°), and the *cis*-1,4-ditosylate, m.p. 98–99.5° (Owens and Robins, m.p. 98–99°).

cis- and *trans*-1,4-cyclohexanediol (purchased from Columbia Organic Chemical Co. and identical to the diol mixture from reduction of 1,4-cyclohexanedione) was quantitatively converted to *cis*- and *trans*-1,4-cyclohexanediol diacetate. V.p.c. analysis[28] of the mixture showed two peaks. The peak at 32.6 min. (relative to the air peak) corresponded to *trans*-1,4-cyclohexanediol diacetate (m.p. 104–104.5°, compared with m.p. 102.5–103.5°, described by Perrin and White).[9] The other peak at 35.0 to 35.3 min. (relative to air) assigned to *cis*-1,4-cyclohexanediol diacetate, was isolated by v.p.c. and its infrared spectrum obtained. The *cis*-1,4-diacetate comprised 51% of the mixture compared to 49% for the *trans*-1,4-diacetate. *cis*- and *trans*-1,3-Cyclohexanediol (purchased from K and K Laboratories, Jamaica 33, N. Y.) was converted to *cis*- and *trans*-1,3-cyclohexanediol diacetates in 95% yield. Since the yield was not quantitative, the diacetate mixture was analyzed.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05; mol. wt., 200. Found: C, 60.18; H, 8.03; mol. wt., 200, 205.

V.p.c. of the 1,3-diacetates also showed two peaks; the first peak (52%) at 29 min. from air could not be confused with either of the 1,4-diacetates, but the second peak (48%), at 35.6 min. from air, could be confused with the *cis*-1,4-cyclohexanediol diacetate. A sample of the 35.6-min. peak was isolated by v.p.c. and compared with the previously isolated *cis*-1,4-cyclohexanediol diacetate. The infrared spectra of these two compounds were completely different.

Reaction of Cyclohexanediol with Hydrobromic Acid.—In a typical experiment, 5.8 g. (0.05 mole) of cyclohexanediol and 50 ml. (0.44 mole) of hydrobromic acid (48%) were combined in a two-necked 100-ml. flask equipped with condenser and thermometer. The mixture was heated on a steam bath for 2 hr. and allowed to stand at room temperature overnight. The reaction mixture was neutralized with dilute sodium hydroxide and extracted with *n*-pentane. The pentane layer was washed with water; the water layers were combined and extracted again with *n*-pentane. Both the pentane layers were combined,

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(27) J. R. Vincent, *J. Org. Chem.*, **3**, 603 (1939).

(28) Obtained with a 2-m. Perkin-Elmer P column plus 3 m. of ethylene glycol succinate on Chromosorb W at 170° and with a flow of 115 cc./min. of helium.

dried over anhydrous calcium chloride, stripped of solvent under water aspirator vacuum, and distilled (95–105°) under vacuum (6.9 mm.). The products were analyzed by v.p.c.[29] and the results shown in Table I.

Reaction of Phosphorus Tribromide with Cyclohexanediol.—In a typical experiment, 11.6 g. (0.10 mole) of cyclohexanediol and 100 ml. of cyclohexane were slurried together in a three-necked 250-ml. flask equipped with dropping funnel, condenser, and magnetic stirrer. To this slurry was added, dropwise, 28.0 g. (0.10 mole) of phosphorus tribromide. After the phosphorus tribromide addition was complete, the mixture was gradually heated with an oil bath. When the temperature reached 85°, evolution of hydrogen bromide was noted and the solid phase started to disappear. Heating was continued to 95° and until hydrogen bromide evolution had ceased. The reaction mixture became cloudy and a small amount of yellow solid precipitated at the bottom of the flask. The reaction mixture was allowed to cool and the cloudy liquid was decanted from the solid and washed repeatedly with a saturated sodium carbonate solution until the aqueous layer remained slightly basic. The water layers were then extracted with cyclohexane; the organic layers were combined, dried over anhydrous calcium chloride, stripped of solvent under water aspirator vacuum, and distilled (97–108°) under vacuum (7.1–9.5 mm.). The products analyzed by v.p.c. are shown in Table II.

Separation of *cis*- and *trans*-1,3 and 1,4-Dibromocyclohexanes.—Preliminary separation of the 1,3- and 1,4-dibromocyclohexanes was accomplished in the following manner. On a 6 cm. × 100 cm. column containing approximately 2750 g. of acid-washed alumina saturated with *n*-pentane were added the 1,3- and 1,4-dibromocyclohexanes. Elution was done with *n*-pentane; 500-ml. fractions (after evaporation of the pentane) were analyzed by v.p.c.[30] Fractions 11 through 17 contained the *trans*-1,3-dibromocyclohexane (**1**) and the *trans*-1,4-dibromocyclohexane (**2**) only. Fractions 18 through 22 contained all four isomers and fractions 23 through 33 contained the *cis*-1,3-dibromocyclohexane (**3**) and the *cis*-1,4-dibromocyclohexane (**4**). Using preparative gas chromatography, the first two and last two isomers were separated from one another. The preparative gas chromatographic unit consisted of four 5-ft. lengths of 0.5-in. o.d. stainless steel tubing joined in series by 0.25-in. o.d. tubing. The 5-ft. lengths were packed with 20% ethylene glycol succinate on acid-washed Chromosorb W, purchased from Wilkens Instrument and Research, Inc., Walnut Creek, Calif. The columns were housed in an oven whose temperature was controlled by three separate electrical resistance heaters. As sample vaporizer, a 0.5-in. Swagelok tee was filled with stainless steel protruded packing, fitted with a rubber septum injection port and heated with an electrical tape. The entire unit was connected in series to the detector and collector of a Perkin-Elmer Model 154 vapor fractometer. Operating the column oven at 150–160° and the same vaporizer at 200° with a helium flow of 490 cc./min., 0.15-ml. mixtures were injected. Retention times for the isomers were in the order of 50–80 min.

***trans*-1,3-Dibromocyclohexane (1).**—This isomer is a liquid having a 13.0-min. retention time from air on a 6-m. analytical column[30] and has the following index of refraction: $n^{25}\text{D}$ 1.5472.

Anal. Calcd. for $C_6H_{10}Br_2$: C, 29.78; H, 4.17; Br, 66.05; mol. wt., 242. Found: C, 29.91; H, 4.32; Br, 66.00; mol. wt., 263.

***trans*-1,4-Dibromocyclohexane (2).**—This isomer is a solid, m.p. 111.5–112°, with a 15.4-min. retention time from air.[30]

Anal. Calcd. for $C_6H_{10}Br_2$: C, 29.78; H, 4.17; Br, 66.05; mol. wt., 242. Found: C, 29.94; H, 4.04; Br, 66.06; mol. wt., 254.

***cis*-1,3-Dibromocyclohexane (3).**—This isomer is a liquid, $n^{25}\text{D}$ 1.5445, and has a 17.2-min. retention time from air.[30]

Anal. Calcd. for $C_6H_{10}Br_2$: C, 29.78; H, 4.17; Br, 66.05; mol. wt., 242. Found: C, 29.95; H, 4.34; Br, 66.04; mol. wt., 250.

***cis*-1,4-Dibromocyclohexane (4).**—This isomer is a solid, m.p. 48°, and has a 21.3-min. retention time from air.[30]

Anal. Calcd. for $C_6H_{10}Br_2$: C, 29.78; H, 4.17; Br, 66.05; mol. wt., 242. Found: C, 29.95; H, 4.36; Br, 66.35; mol. wt., 254.

Reaction of 3-Bromocyclohexene with Aqueous Hydrobromic Acid.—3-Bromocyclohexene [b.p. 52.5–54° (7–9 mm.); $n^{20}\text{D}$ 1.5303] was prepared from cyclohexene and N-bromosuccinimide.[31] To a flask containing 3 ml. (0.027 mole) of 47–49% aqueous hydrobromic acid was added 0.8 g. (0.005 mole) of 3-bromocyclohexene. The flask was stoppered, heated (65°), and shaken for 7 hr. The organic phase was analyzed by v.p.c. as previously described.[30] The analysis is shown in Table IV.

TABLE IV

PRODUCTS FROM 3-BROMOCYCLOHEXENE AND AQUEOUS HYDROBROMIC ACID

Dibromocyclohexane isomer	Per cent based on only 1,3- and 1,4-dibromides
trans-1,3	23
trans-1,4	17
cis-1,3	43
cis-1,4	17

V.p.c. analysis also showed that phenylcyclohexane and 1,2-dibromocyclohexane made up slightly over half the total product.

Dipole Moment Measurements.—A Sargent oscillometer was used for measurement of dielectric constant of solutions after standardization with known solvents. A span of 3000 dial units was equivalent to a change of 0.1 in dielectric constant. The error in dial units was ±25 units. This means that the observed dielectric constant was good to ±0.001. The calculation of $P_{2\infty}$ shown was that used by Hedestrand.[11]

$$P_{2\infty} = A(M_2 - B\beta) + C\alpha$$

$$A = \frac{\epsilon_1 - 1}{\epsilon_1 - 2};\ B = M_1/d_1;\ C = 3\ M_1/(\epsilon_1 + 2)^2 d_1$$

$$\epsilon_{12} = \epsilon_1 + \alpha f_2 \qquad d_{12} = d_1 + \beta f_2$$

ϵ_1 = dielectric constant of pure solvent
ϵ_{12} = dielectric constant of solution
d_1 = density of pure solvent
d_{12} = density of solution
f_2 = mole fraction of solute in solution
M_1 = molecular weight of solvent
M_2 = molecular weight of solute

Heptane was used as solvent for all the dipole moment measurements since data in this solvent agrees with results in carbon tetrachloride.[12,17] A typical result is shown for *cis*-1,4-dibromocyclohexane in Table V.

TABLE V

CALCULATION OF α, β, AND $P_{2\infty}$ FOR *cis*-1,4-DIBROMOCYCLOHEXANE IN HEPTANE

f_2	ϵ	d
0.00000	1.917	0.6783
0.00468	1.944	0.6834
0.00843	1.964	0.6889
0.01681	2.024	0.6952
0.02395	2.066	0.7103
α = 6.286	β = 0.9388	$P_{2\infty}$ = 216.97

Computation of the dipole moment required molar refraction data. A summation of group refractions, 43.24, was used since this varied only by 0.3% from the molar refraction calculated from index of refraction and density of the dibromide mixture.

$$d_4^{24.5}\ 1.7714 \qquad n^{24.5}\text{D}\ 1.5476$$

$$R_\text{D} = \frac{n^2 - 1}{n^2 + 2}\frac{(\text{mol. wt.})}{d} = \frac{1.3951}{4.3951} \cdot \frac{242}{1.7714} = 43.37$$

The dipole moments were calculated from the Debye equation.

$$\mu = 0.01281 \times 10^{-18}[(P_{2\infty} - R_\text{D})T]^{1/2}$$

The results are shown in Table VI (p. 2244).

Theoretical Calculation of Dipole Moments.—Using the cyclohexane model of Corey and Sneen[14] shown in Fig. 4, the

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[29] A Perkin-Elmer 3 m. × 1/4 in. Column P at 160° and 115 cc./min. helium flow was used.

[30] Analysis done with a 6 m. × 0.25 in. column packed with 20% ethylene glycol succinate on acid-washed Chromosorb W at 136° and 130 cc./min. helium flow.

[31] K. Ziegler, A. Spath, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann.*, **551**, 80 (1942).

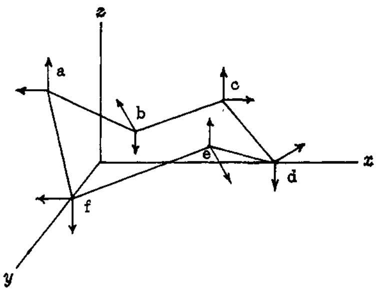

Fig. 4.—Cyclohexane.

TABLE VI

SUMMARY OF DIPOLE MOMENT DATA

Dibromo-cyclohexane	$P_{2\infty}$	R_D	μ, D.
trans-1,3	141.52	43.24	2.19
trans-1,4	49.36	43.24	0.55
cis-1,3	139.67	43.24	2.17
cis-1,4	216.97	43.24	2.92

coordinates of the atoms are listed in Table VII and the unit vectors are shown in Table VIII. The latter calculation is patterned after Wilcox's work.[13]

TABLE VII

COORDINATES OF THE ATOMS

Atom	x	y	z
a	−0.729	0	+0.521
b	0	−1.266	0
c	+1.46	−1.266	+0.521
d	+2.19	0	0
e	+1.46	+1.266	+0.521
f	0	+1.266	0

TABLE VIII

UNIT VECTORS

Position	i (x)	j (y)	k (z)
a (axial)	0	0	+1.00
a (equatorial)	−0.944	0	−0.330
b (axial)	0	0	−1.00
b (equatorial)	−0.4706	−0.8156	−0.330
c (axial)	0	0	+1.00
c (equatorial)	+0.4706	−0.8156	−0.330
d (axial)	0	0	−1.00
d (equatorial)	+0.944	0	+0.330
e (axial)	0	0	+1.00
e (equatorial)	+0.4706	+0.8156	−0.330
f (axial)	0	0	−1.00
f (equatorial)	−0.4706	+0.8156	+0.330

From Tables VI–VIII, the dipole moment and the group separations can be calculated.

$$\text{Total moment} = [(i\text{-moment})^2 + (j\text{-moment})^2 + (k\text{-moment})^2]^{1/2}$$

$$\text{Group separation} = [(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2]^{1/2}$$

Thus for *trans*-1,3-dibromocyclohexane which we can designate as atoms a (axial), e (equatorial), we have the following calculation,[13] assuming a C–Br bond moment of 1.91 D.

$$i\text{-moment} = 0.4706 \times 1.91 = 0.899 \text{ D.}$$
$$j\text{-moment} = 0.8156 \times 1.91 = 1.558 \text{ D.}$$
$$k\text{-moment} = (1.00 \times 1.91) - (0.330 \times 1.91) = 1.638 \text{ D.}$$

$$\text{Total moment} = [(0.399)^2 + (1.558)^2 + (1.638)^2]^{1/2} = (4.873)^{1/2} = 2.21 \text{ D.}$$

If one assumes C–Br distance as 1.91 Å. the calculation of group separation for the 1,3-diaxial conformation is as follows using atoms f (axial) and d (axial).

$$\text{(f)}\ x_1 = 0.00 \qquad y_1 = 1.266 \qquad z_1 = -1.00 \times 1.91 = -1.91$$
$$\text{(d)}\ x_2 = 2.19 \qquad y_2 = 0 \qquad z_2 = -1.00 \times 1.91 = -1.91$$

$$\text{Group separation} = [(2.19)^2 + (1.266)^2 + (-1.91 + 1.91)^2]^{1/2}$$
$$\text{Group separation} = [6.399]^{1/2} = 2.53 \text{ Å.}$$

N.m.r.—Spectra were recorded preliminarily with a Varian A-60 proton resonance spectrometer. Variable temperature n.m.r. experiments were carried out using a Varian HR-60 spectrometer equipped with a Model V-4340 variable temperature probe, a slow-sweep unit of our own construction, and a commercial X-Y recorder. Cooling was manually controlled by passing nitrogen from a cylinder through a coil of copper tubing immersed in either a Dry Ice or a liquid nitrogen bath. Needle valves, both in series with, and by-passing the coil provided stable smooth manual control of probe temperature. To obtain spectra below room temperature, the samples of dibromocyclohexanes were dissolved in carbon disulfide, approximately 50% by volume. A small amount of tetramethylsilane in the sample solution served as an internal reference for measurement of chemical shifts. The internal reference also provided an inherently sharp spectral line to facilitate optimization of magnetic field homogeneity at each temperature level. At elevated temperatures, the solvent was omitted and a small amount of *p*-dichlorobenzene was dissolved in the dibromocyclohexane samples to facilitate homogeneity adjustments.

Temperatures were observed generally by means of the thermocouple normally located within the dewar-type receiver coil assembly V-4331-THR. However, in critical temperature regions true temperatures of the sample were obtained from a second thermocouple inserted directly into the sample tube. With this general technique, the coalescence temperature of the methyl group "doublet" in the spectrum of N,N-dimethylformamide was determined as 119° *vs.* lit. value of 117°.[32]

Acknowledgment.—The authors are indebted to Mr. John H. Surridge for his design of the preparative gas chromatograph and his technical assistance in the separation of the dibromocyclohexanes. The authors also wish to thank Dr. P. V. Smith for reviewing and correcting this manuscript.

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(32) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956)