Conformational Analysis. The Trifluoromethyl Group[1,2]

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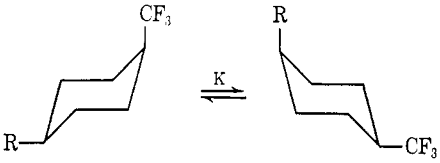
Abstract: The conformational preference of the trifluoromethyl group has been determined by ^{19}F nuclear magnetic resonance spectroscopy and is found to fall in the range 2.4–2.5 kcal/mole. Two nmr methods were applied and gave practically identical results: (a) based on differences in chemical shifts between the conformationally homogeneous systems, *cis*- and *trans*-4-*t*-butyltrifluoromethylcyclohexane, and the mobile system, *cis*-4-methyltrifluoromethylcyclohexane; and (b) by freezing of the *cis*-4-methyltrifluoromethylcyclohexane equilibrium and measuring the areas under the trifluoromethyl signals from each of the chair conformations. $-\Delta G_{CF_3}$ is found to be independent of the solvent. A method of assigning configurations to carboxyl functions attached to the cyclohexane ring is suggested.

The area of conformational analysis devoted to determining conformational preferences ($-\Delta Gx$) of substituents attached to the cyclohexane ring has been actively explored during the past decade,[3] and the usefulness of such determinations is well documented.[4,5] Of the substituents studied the trifluoromethyl group is notably missing; the only pertinent work[6] is on ^{19}F nuclear magnetic resonance (nmr) spectra of the 4-trifluoromethyldecafluorocyclohexanes and indicates that the CF_3 group exists predominantly in the equatorial configuration. Unlike other symmetrical substituents so far examined, *e.g.*, CH_3, NR_3^+, and CMe_3, the trifluoromethyl group could, when orientated axially, exhibit attractive H–F London forces which may influence its conformational preference by partially offsetting steric repulsions. Estimates *a priori* suggest that in the absence of London attractions, trifluoromethyl is not much "larger" than methyl since fluorine itself has a small conformational preference (0.2 kcal/mole).[7,8] Nmr spectroscopy[3b] seemed eminently suited to the determination of $-\Delta G_{CF_3}$, especially in view of the possibility of using both proton and fluorine resonances; moreover, the large chemical shifts associated with the latter should provide accurate analytical data.[9]

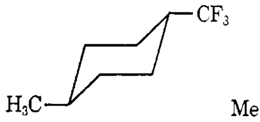
Results

The recently described method[10] of converting carboxylic acids to their trifluoromethyl derivatives in high yield by treatment with sulfur tetrafluoride provides a good route to the desired compounds II–V, particularly as the stereochemistry of the precursor acids is well defined, and Cram and Wingrove[11] have shown that under mild conditions the sulfur tetrafluoride reaction is stereospecific. Fluorinations were conducted at 70° at which temperature the reactions, although slow, proceeded with complete stereospecificity. At 130°, conversion of carboxyl into trifluoromethyl is rapid[10] but significant epimerization occurred under these conditions. Presumably epimerization under the more drastic conditions is effected at the intermediate acid fluoride stage.[12] Trifluoromethylcyclohexane and quantities of mixed *cis*- and *trans*-4-methyltrifluoromethylcyclohexane were obtained by hydrogenation of the corresponding aromatic compounds.

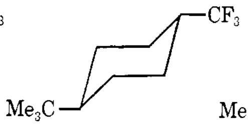


Ia, R = H
IIa, R = CH_3

Ie, R = H
IIe, R = CH_3



III



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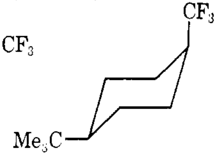

V

Table I summarizes details of the ^{19}F magnetic resonance spectra of the trifluoromethylcyclohexanes I–V dissolved in solvents of different polarities and hydrogen-bonding capability. These data lead to the equilibrium constant K for the equilibrium IIa $\rightleftharpoons$ IIe (from $K = (\phi a - \phi)/(\phi - \phi e)$) and hence the free energy difference, $-\Delta G_0$, between the conformers IIa and IIe of *cis*-4-methyltrifluoromethylcyclohexane (Table II). Using 1.7 kcal/mole for the value of $-\Delta G_{CH_3}$ leads to the conformational preference of trifluoromethyl in the different solvents (Table II).

As expected, the fluorine signal appear as doublets; values of $J_{F,H}$ (calculated to ±0.5 cps) are included in

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(1) Reported, in part, at the 3rd National Convention of the Royal Australian Chemical Institute, Canberra, Australia, Aug 15–18, 1966.

(2) For a preliminary account of some of the results see E. W. Della, *Tetrahedron Letters*, 3347 (1966).

(3) For recent reviews see (a) E. L. Eliel, *Angew. Chem.*, **77**, 784 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 761 (1965); (b) N. C. Franklin and H. Feltkamp, *Angew. Chem.*, **77**, 798 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 774 (1965); (c) J. McKenna, "Conformational Analysis of Organic Compounds," The Royal Institute of Chemistry, London, England, Lecture Series, 1966, No. 1.

(4) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965.

(5) M. Hanack, "Conformation Theory," Academic Press Inc., New York, N. Y., 1965.

(6) (a) J. Homer and L. F. Thomas, *Trans. Faraday Soc.*, **59**, 2431 (1963); (b) J. Feeney and L. H. Sutcliffe, *J. Phys. Chem.*, **65**, 1894 (1961).

(7) (a) Reference 4, p 436. (b) See also F. A. Bovey, E. W. Anderson, F. P. Hood, and R. L. Kornegay, *J. Chem. Phys.*, **40**, 3099 (1964).

(8) E. L. Eliel and R. J. Martin, unpublished observations communicated to the author (by R. J. M.)

(9) (a) J. D. Roberts, *Chem. Brit.*, **2**, 529 (1966), and references therein; (b) S. L. Spassov, D. L. Griffith, E. S. Glazer, K. Nagarajan, and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 88 (1967).

(10) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

(11) D. J. Cram and A. S. Wingrove, *ibid.*, **86**, 5490 (1964).

(12) *Cf.* results on equilibration of acid chloride, ref 4, p 442.

Table I. ^{19}F Chemical Shifts (ppm) and $J_{F,H}$ Coupling Constants (cps) of the Trifluoromethylcyclohexanes (27°)

Trifluoromethyl-cyclohexane		$CFCl_3$[a]	$CHCl_3$[b]	Cyclo-hexane[b]	Ace-tone[b]	Meth-anol[b]
Unsubstituted	ϕ	75.04	74.78	75.25	74.03	74.50
	J	7.8	8.0	7.7	8.3	8.0
cis-4-Methyl	ϕ	73.16	72.97	73.30	72.24	72.58
	J	8.1	8.2	7.9	8.7	8.2
trans-4-Methyl	ϕe	74.74	74.49	74.91	73.81	74.22
	J	7.4	7.4	7.5	8.0	7.6
trans-4-*t*-Butyl	ϕe	74.78	74.56	75.02	73.86	74.23
	J	7.4	7.4	7.2	8.0	7.8
cis-4-*t*-Butyl	ϕa	67.39	67.19	67.57	66.58	66.88
	J	11.1	11.1	10.9	11.3	11.5

[a] Concentration 3 *M*. Chemical shift has the symbol ϕ^*; see G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959). [b] Concentration 8–10%.

Table II. Conformational Energy of Trifluoromethyl in Various Solvents (27°)

Solvent	K[a]	$-\Delta G_0$,[a,b] kcal/mole	$-\Delta G_{CF_3}$, kcal/mole
Fluorotrichloromethane	3.56	0.8	2.5[c]
Chloroform	3.64	0.8	2.5[c]
Cyclohexane	3.33	0.7	2.4[c]
Cyclohexane	2.15	0.5	2.2[d]
Acetone	3.50	0.8	2.5[c]
Methanol	3.45	0.7	2.4[c]

[a] For equilibrium IIa ⇌ IIe. [b] $-\Delta G_0 = -\Delta G_{CF_3} + \Delta G_{CH_3}$. [c] This work. [d] Infrared value, ref 2.

Table I. Whereas the ^{19}F absorptions observed in the spectra of compounds I–IV appeared as sharp doublets, that due to *cis*-4-*t*-butyltrifluoromethylcyclohexane showed additional fine structure arising presumably from long-range coupling of fluorine and the 3,5- and/or 2,6-diaxial protons. Long-range coupling between fluorine and hydrogen has been observed in many instances,[9,13] particularly in systems where the coupled atoms are separated by five σ bonds. Little information has appeared on 4-bond hydrogen–fluorine coupling in saturated compounds. Further work with appropriately deuterated analogs of *cis*-4-*t*-butyltrifluoromethylcyclohexane is being undertaken in order to elucidate the origin of the observed coupling.

Positions of ^{19}F signals are recorded as upfield shifts from fluorotrichloromethane and are calculated to within ±0.02 ppm from eight upfield and downfield sweeps. Calibration was effected by the side-band technique. Chemical shifts in all solvents except fluorotrichloromethane may be regarded as those at infinite dilution (ϕ)[14] in view of the dilute solutions used. The shifts in fluorotrichloromethane were measured in concentrated solution (3 *M*) and are designated as ϕ^* values. Table III lists $\phi^*_{CF_3}$ of selected compounds dissolved in fluorotrichloromethane (3 *M*) over a range of temperatures, from which the corresponding free energy differences between IIa and IIe may be evaluated (Table IV). Derivation of $-\Delta G_{CF_3}$ at the various temperatures, however, requires the conformational preference of methyl at each temperature to be known. Armitage, Kenner, and Robinson[15] have shown that $-\Delta G_{CH_3}$ is essentially independent of temperature, a result supported by theoretical considerations,[16] and accordingly the value 1.7 kcal/mole is taken to be constant over the range considered. The values of $-\Delta G_{CF_3}$ follow (Table IV). No attempt has been made to dissect the free energy term into its enthalpy and entropy components as the data are not sufficiently accurate.

Table III. Variation of ^{19}F Trifluoromethyl Resonance with Temperature

Trifluoromethyl-cyclohexane[a]	Chemi-cal shift	−73°	−56°	27°	50°
cis-4-Methyl	ϕe*	74.50	73.65[b]	73.16[b]	73.11[b]
	ϕa*	66.63			
trans-4-*t*-Butyl	ϕe*	74.44	74.46	74.78	74.87
cis-4-*t*-Butyl	ϕa*	66.53	66.74	67.39	67.64

[a] Concentration 3 *M* ($CFCl_3$ solvent). [b] Coalesced signal, ϕ^*.

Table IV. Conformational Energy of Trifluoromethyl at Several Temperatures ($CFCl_3$ solvent)

Temp, °C	K[a]	$-\Delta G_0$,[a,b] kcal/mole	$-\Delta G_{CF_3}$, kcal/mole
−73	8.25	0.8	2.5[c]
−56	8.53	0.9	2.6[d]
27	3.56	0.8	2.5[d]
50	3.11	0.7	2.4[d]

[a] For equilibrium IIa ⇌ IIe. [b] $-\Delta G_0 = -\Delta G_{CF_3} + \Delta G_{CH_3}$. [c] From peak areas. [d] From chemical shift differences.

The low-temperature measurements are of particular interest. Controlled cooling of *cis*-4-methyltrifluoromethylcyclohexane showed partial broadening of the ^{19}F doublet (−27°), extreme broadening (−56°), and finally separation of the time-averaged signal into two peaks (−73°), one a reasonably well-defined doublet corresponding in position to that found in *trans*-4-*t*-butyltrifluoromethylcyclohexane and hence due to IIe, the other a somewhat broader signal having a chemical shift very close to that in *cis*-4-*t*-butyltrifluoromethylcyclohexane and accordingly attributed to IIa (Table III).[17] It may be seen that $\phi^*_{CF_3}$ in each conformer of *cis*-4-methyltrifluoromethylcyclohexane practically coincides with the chemical shift of the equatorial and axial trifluoromethyl group, respectively. The very good agreement observed, less than 0.2 ppm, justifies the assumption (see below) that the 4-alkyl substituent has no influence on the position of the axial CF_3 resonance. Measurement of the areas under the resolved peaks gave K as 8.25 and hence $-\Delta G_{CF_3}$ as 2.5 kcal/mole.

Discussion

As noted previously[2] (and as indicated above) evaluation of the constant for the equilibrium Ia ⇌ Ie is not feasible since the position of equilibrium lies almost completely to the right.[6] Attention was therefore directed to the equilibrium (IIa ⇌ IIe) in which the *cis*-4-methyl group was expected to counteract to some extent the influence of the bulky trifluoromethyl substituent, giving a more balanced equilibrium.[2,18] The deter-

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(13) See P. C. Myhre, J. W. Edmonds, and J. D. Kruger, *J. Am. Chem. Soc.*, **88**, 2459 (1966), for leading references.

(14) See Filipovich and Tiers, footnote *a*, Table I.

(15) B. J. Armitage, G. W. Kenner, and M. J. T. Robinson, *Tetrahedron*, **20**, 747 (1964).

(16) E. L. Eliel and T. J. Brett, *J. Am. Chem. Soc.*, **87**, 5039 (1965).

(17) Coalescence temperature found to be approximately −62°.

(18) Reference 4, p 78.

mination of $-\Delta Gx$ values from a study of the conformational equilibrium of *cis*-4-methylcyclohexyl-X, the preferable method[18] for examples where $-\Delta Gx > 0.85$ kcal/mole, suffers from the disadvantage that additivities of conformational free energies must be assumed. In most recorded cases, however, this assumption appears to be valid,[3a,4,19] particularly in the 1,4 series,[20] and additivity has been assumed in this work.

One of the successful nmr methods[21] of determining conformational preferences is based on the relationship $K = (\delta a - \delta)/(\delta - \delta e)$, where δa and δe refer to chemical shifts of the methine proton in the conformationally biased systems *cis*- and *trans*-4-*t*-butylcyclohexyl-X, and δ that in the mobile cyclohexyl-X. These protons could not be employed here because the relevant signals in II, IV, and V were hidden under the ring proton envelope. Appropriate ^{19}F magnetic resonances, however, could be used instead (Table I). One of the questions associated with the use of the equation above is whether δa and δe do in fact represent the positions of the equatorial and axial methine proton, respectively, in the conformationally mobile system, which at room temperature shows a time-averaged signal. As seen in Table I, the chemical shifts (ϕe) of the trifluoromethyl group in the *trans*-4-alkyltrifluoromethylcyclohexanes (III and IV) are remarkably close, if not coincident. Both III and IV would be expected to exist exclusively in the conformations shown, showing that the nature of the 4-alkyl substituent has no apparent effect on the position of equatorial CF_3 resonance. The latter is shifted slightly from that in trifluoromethylcyclohexane, although not in the direction expected. Allowing for a small contribution of Ia to the equilibrium Ia $\rightleftharpoons$ Ie, the time-averaged ^{19}F signal of trifluoromethylcyclohexane should occur close to ϕe and between the extremes defined by ϕe (from IV) and ϕa (from V). The most plausible reason accounting for the "anomalous" behavior of I is that the substituent in *trans*-4-substituted trifluoromethylcyclohexanes does exert a mild influence on the position of the CF_3 resonance. Where no noticeable difference in chemical shift occurs when the substituent is methyl or *t*-butyl, replacement of R by H produces a small upfield shift of the CF_3 signal.

On the basis of the results obtained from the *trans*-4-alkyltrifluoromethylcyclohexanes, it seemed reasonable that the position of axial trifluoromethyl resonance would similarly be unaffected by the type of 4-alkyl substituent, and confirmation for this appears above. In any case the rather large difference in chemical shift between ϕe, ϕa, and ϕ tends to minimize any slight errors in their absolute values.

The equilibrium constant, K, obtained from peak areas at −73° is in excellent agreement with that determined at −56° by the chemical shift method. The correlation of conformational preferences derived from the nmr and infrared methods (Table II) is not as good although the values are still quite comparable. It is suggested that the value determined by infrared spectroscopy is a little low[22] and that $-\Delta G_{CF_3}$ lies between 2.4 and 2.5 kcal/mole at 27°. This is in accord with the result expected from a consideration of nonbonded repulsive interactions apparent in molecular models of IV and V together with a comparison of the trifluoromethyl, methyl, and *t*-butyl groups, and the relative size of hydrogen, fluorine, and methyl. Interestingly, $-\Delta G_{CF_3}$ is independent of the solvent. It was thought that hydrogen donor (and good solvating) solvents such as methanol might have increased the effective bulk of the CF_3 substituent, or alternatively have stabilized the equatorially placed group, giving a higher $-\Delta G$ value. Trifluoromethyl evidently behaves in a similar way to polar substituents such as the halogens whose conformational preferences are unaffected by protic solvents.[23]

The magnitude of the chemical shift difference of fluorine resonances in axial and equatorial trifluoromethyl groups suggests a method of assigning configurations to carboxyl substituents at centers of unknown stereochemistry in rigid systems. Conversion of the acid into its trifluoromethyl derivative with sulfur tetrafluoride is a relatively facile process and a reasonably selective one as other functional groups such as C=C, OR, phenyl, and COOR are not attacked by the reagent at moderate temperatures. The configuration of the derived CF_3 group may then be deduced from its fluorine nmr spectrum. The method would be analogous to one which has been used[24] in assigning the configuration of an aldehyde group on the basis of the different proton chemical shifts of the equatorial and axial formyl substituent.

Experimental Section

Boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord Model 237. Preparative vapor phase chromatography was performed on a Perkin-Elmer vapor fractometer, Model 154-D, or a Wilkens Autoprep, Model 705. Analytical vpc was effected by a Griffin and George chromatograph. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne, Victoria. Proton magnetic resonance spectra were measured on the Varian Associates Model A60-A spectrometer (TMS internal standard). Fluorine magnetic resonance spectra were determined on the Varian DP-60 instrument operated at 56.4 Mcps. Calibration was effected by the side-band technique with the use of a Muirhead-Wigan Decade audio oscillator ($CFCl_3$ internal standard). Variable-temperature work was performed with the Varian temperature probe with dewar insert.

Trifluoromethylcyclohexane (I). Benzotrifluoride (8.0 g, 0.055 mole) and Adams' catalyst (0.2 g) in 60 ml of ethanol were shaken under a hydrogen atmosphere (45 psi) for 14 hr when the absorption of hydrogen ceased. Catalyst was filtered and the filtrate poured into 150 ml of water which was extracted with three 25-ml portions of ether. The combined ether extracts were washed with water (three 15-ml portions), dried ($MgSO_4$), and distilled through a short fractionating column to yield 5.2 g (65%) of a colorless oil, bp 101–101.5° (680 mm), n^{22}D 1.3752 (lit.[25] bp 105.8° (760 mm), n^{25}D 1.3739). Infrared bands were found at 684 (ϵ 68, cyclohexane)[2] and 1348 cm^{-1} (neat). ^{19}F magnetic resonances are recorded in Tables I and III.

***cis*-4-Methyltrifluoromethylcyclohexane (II). Method A.** A 70-ml copper bomb was charged with 5.0 g (0.035 mole) of *cis*-4-methylcyclohexanecarboxylic acid[26] and 10 g (0.09 mole) of sulfur tetrafluoride.[10] The bomb was heated at 70° for 10 days, cooled, and vented in a fume hood. The violet product was extracted with 10 ml of pentane, washed with water (two 30-ml portions),

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(19) N. C. Franklin and H. Feltkamp, *Tetrahedron*, **22**, 2801 (1966).

(20) E. L. Eliel, S. H. Schroeter, T. J. Brett, F. J. Biros, and J-C. Richer, *J. Am. Chem. Soc.*, **88**, 3327 (1966).

(21) E. L. Eliel, *Chem. Ind.* (London), 568 (1959); E. L. Eliel and M. H. Gianni, *Tetrahedron Letters*, 97 (1962).

(22) Possibly due to variation of the extinction value of equatorial CF_3 bands over a wide range of concentration.

(23) E. L. Eliel, *Angew. Chem.*, **77**, 765 (1965).

(24) (a) R. A. Laidlaw and J. W. W. Morgan, *J. Chem. Soc.*, 644 (1963); (b) T. J. King and J. P. Yardley, *ibid.*, 4308 (1961), and ref 9 therein.

(25) J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).

(26) E. L. Eliel, H. Haubenstock, and R. V. Acharya, *ibid.*, **83**, 2351 (1961).

and dried ($MgSO_4$) and the solvent evaporated to give 4.7 g of a crude product which by vpc (12-ft SE-52, 41°) was shown to contain approximately 12% of the corresponding acid fluoride. Distillation gave 2.9 g (50%) of II, bp 115–116° (680 mm). Characteristic bands in the infrared were located at 692 (ε 43, cyclohexane),[2] 711 (ε 9, cyclohexane),[2] and 1315 cm^{-1} (neat). ^{19}F magnetic resonance spectra data are recorded in Tables I and III. *Anal.* Calcd for $C_8H_{13}F_3$: C, 57.82; H, 7.88; F, 34.30. Found: C, 57.99; H, 7.86; F, 34.2.

Method B. *p*-Trifluoromethylbenzyl bromide[27] (9.0 g, 0.038 mole) and lithium aluminum hydride (0.8 g, 0.021 mole) in 30 ml of tetrahydrofuran were heated under reflux for 1 hr. On cooling, ice-cold water was added dropwise, and the metal hydroxides were dissolved in 2 *N* sodium hydroxide (25 ml). The organic layer was added to 60 ml of ether, washed with water (four 15-ml portions) and saturated sodium chloride solution (one 15-ml portion), and dried ($MgSO_4$). Distillation through an efficient fractionating column yielded 4.8 g (80%) of *p*-methylbenzotrifluoride, bp 128–129° (760 mm). The infrared spectrum contained intense bands at 1130, 1170, and 1340 cm^{-1} (neat). The pmr spectrum was identical with that published.[28] *Anal.* Calcd for $C_8H_7F_3$: C, 60.00; H, 4.41. Found: C, 60.25; H, 4.74. *p*-Methylbenzotrifluoride (4.4 g) in 10 ml of ethanol was hydrogenated using the procedure described for benzotrifluoride. The product (4.2 g) was shown by vpc (conditions as above) to consist of a 4:1 mixture of *cis*- and *trans*-4-methyltrifluoromethylcyclohexane which was separated by preparative vpc (12-ft, 20% Apiezon L, 108°) into the pure components (2.5 g, II; 0.5 g, III), the former being identical with the sample of *cis*-4-methyltrifluoromethylcyclohexane obtained by method A.

trans-**4-Methyltrifluoromethylcyclohexane (III).** A 2:1 mixture of *cis*- and *trans*-4-methylcyclohexanecarboxylic acid[26] (8.5 g, 0.06 mole) was converted to a mixture (2:1) of the corresponding trifluoromethylcyclohexanes (7.5 g) by reaction with 20.5 g (0.19 mole) of sulfur tetrafluoride under the conditions described above. Preparative vpc (12-ft, 20% Apiezon L, 108°) yielded the pure (99%) *trans* epimer (1.2 g), bp 118–119° (760 mm), identical in all respects with the sample obtained from method B above. Characteristic bands were present in the infrared at 692 (ε 62, cyclohexane)[2] and 1340 cm^{-1} (neat). Fluorine magnetic resonance data are collected in Tables I and III. *Anal.* Calcd for $C_8H_{13}F_3$: C, 57.82; H, 7.88; F, 34.30. Found: C, 57.50; H, 7.53; F, 34.8.

trans-**4-*t*-Butyltrifluoromethylcyclohexane (IV).** *trans*-4-*t*-Butylcyclohexanecarboxylic acid[29] (4.3 g, 0.024 mole) was similarly treated with 8 g (0.074 mole) of sulfur tetrafluoride to give 3.8 g (76%) of IV, bp 85–86° (34 mm); n^{20}D 1.4082. The infrared spectrum contained characteristic bands at 687 (ε 62, cyclohexane),[2] 1250, and 1340 cm^{-1} (neat). ^{19}F magnetic resonance spectra details are included in Tables I and III. *Anal.* Calcd for $C_{11}H_{19}F_3$: C, 63.44; H, 9.20; F, 27.36. Found: C, 63.40; H, 9.27; F, 27.4.

cis-**4-*t*-Butyltrifluoromethylcyclohexane (V).** *cis*-4-*t*-Butylcyclohexanecarboxylic acid[29] was treated with 10 g (0.10 mole) of sulfur tetrafluoride as described previously, to give 6.8 g of oil which by vpc (12-ft SE-52, 80°) was shown to contain V contaminated with intermediate acid fluoride (*ca.* 10%). The latter was removed by distillation which gave 4.1 g (57%) of *cis*-4-*t*-butyltrifluoromethylcyclohexane, bp 89–90° (37 mm), 70–72° (18 mm); n^{20}D 1.4119. Characteristic bands in the infrared were located at 703 cm^{-1} (ε 31, cyclohexane),[2] 1225, and 1292 cm^{-1} (neat). The ^{19}F magnetic resonance spectra data are recorded in Tables I and III. *Anal.* Calcd for $C_{11}H_{19}F_3$: C, 63.44; H, 9.20; F, 27.36. Found: C, 63.49; H, 8.96; F, 27.6. Repetition of the above reaction at 125–130° for 24 hr gave a product (85% yield) which by vpc (conditions as above) was shown to be uncontaminated with acid fluoride, but which consisted of a mixture of *cis*-4-*t*-butyltrifluoromethylcyclohexane (retention time 13.9 min) and its *trans* epimer (12.7 min).

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(27) H. B. Hass and M. L. Bender, *J. Am. Chem. Soc.*, **71**, 1768 (1949).

(28) "Nmr Spectra Catalog," Varian Associates, Vol. I, Palo Alto, Calif., 1962, Spectrum No. 190.

(29) H. H. Lau and H. Hart, *J. Am. Chem. Soc.*, **81**, 4897 (1959).

Conformational Analysis of Tritolylphosphines[1]

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Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received April 3, 1967*

Abstract: The dependence of dipole moments and ultraviolet absorption spectra on constitution in the series tris(4-methylphenyl)phosphine (**1**), tris(3-methylphenyl)phosphine (**2**), and tris(2-methylphenyl)phosphine (**3**) has been accounted for by a model in which the C–P–C bond angle remains constant at 102° while the angle of torsion around the phosphorus–phenyl bond varies with the position of the substituent methyl group. The present interpretation is at variance with a previous conclusion in which this dependence was rationalized by invoking a variation in the C–P–C bond angle.

In a recent study, Schindlbauer[2] observed the dependence of dipole moments and absorption spectra on constitution in the series of isomeric tritolylphosphines which is reported in Table I, and from these findings concluded that the C–P–C bond angle varies as indicated in Table I. The spread in bond angles was presumed to arise from repulsive interaction effects which increase in the series **1** to **3**.

The extraordinary flattening of the phosphorus pyramid claimed[2] for **3** (see Table I) led us to reexamine Schindlbauer's calculations. In a molecule R_3P with threefold symmetry, assuming that the observed moment μ acting along the C_3 axis equals the resultant of the partial moments, the relation between μ and the group moments μ_R is given by

$$\mu = 3\mu_R \cos\theta \qquad (1)$$

where θ is the angle between μ and μ_R (see Figure 1).

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(2) H. Schindlbauer, *Monatsh. Chem.*, **96**, 1793 (1965).