chloride, n_D^{25} 1.5939 (lit.[6] n_D^{25} 1.5937), was obtained by two partial freezings of distilled material, b.p. 151–152.5° (10 mm.), and was stored, frozen, in small vials.

Magnesium perchlorate (Anhydrone) and *perchloric acid* were commercial reagent-grade materials, used as supplied. *Lithium perchlorate, sodium perchlorate* and *ammonium perchlorate* were derived from commercial reagent-grade hydrous salts by drying to constant weights at the appropriate temperatures.

Tetrabutylammonium bromide, m.p. 117–118° (lit.[7] m.p. 119.4°), and *tetrabutylammonium chloride*, m.p. 52–54° sealed cap., were each prepared by stirring a suspension of tetrabutylammonium iodide (25 g.) with a 10% excess of the appropriate silver halide in water (150 ml.) until a few drops of the solution no longer gave a brown precipitate (tetrabutylammonium triiodide) on addition to acidic aqueous sodium nitrite solution. The mixture was filtered from the precipitated silver halides, saturated with hydrogen sulfide, filtered again to remove traces of silver sulfide, and then evaporated to dryness under reduced pressure and finally at 1 mm. over Anhydrone. The anhydrous salts yielded good halogen analyses.

Anal. Calcd. for $C_{16}H_{36}BrN$: Br, 24.79. Found: Br, 24.72, 24.79. Calcd. for $C_{16}H_{36}ClN$: Cl, 12.76. Found: Cl, 12.81, 12.67.

Tetrabutylammonium perchlorate was prepared as described,[8] purified and isolated as with the tetrabutylammonium halides, had m.p. 205–206° (lit.[8] m.p. 207°), and contained *ca.* 1% perchloric acid by acidimetry.

Anal. Calcd. for $C_{16}H_{36}ClNO_4$: Cl, 10.37. Found: Cl, 10.43.

The anhydrous salts were stored in a desiccator over Anhydrone.

Kinetic measurements. The solvent, 10 parts of water to 90 parts of bis(2-ethoxyethyl) ether, was prepared from the components on a weight basis as required for each kinetic run. Each kinetic solution was prepared by diluting weighed amounts of benzhydryl chloride and anhydrous salt to the mark in a volumetric flask with freshly prepared solvent. The solutions were all 0.100 ± 0.001 molar in benzhydryl chloride.

The rates of development of acid were followed as described previously[3] to *ca.* 5% reaction. Large-scale plots of acid concentration *vs.* time were constructed, smooth curves were drawn through the points with the aid of a spline and first-order specific rate constants, k, were calculated according to equation 1 at regular successive intervals of $\Delta(H^+)$

$$k = \Delta(H^+)/(RCl)\Delta t \qquad (1)$$

and Δt such that *ca.* 8 values of k were obtained from each curve. For each run, the initial first-order specific rate constant, k_0, was obtained by extrapolation of the k values to 0% reaction. These extrapolations involved, within experimental error, zero slope for all runs except those with tetrabutylammonium bromide as the added salt. In these runs, values of k rose steadily to a limiting value of 1.36 × 10^{-6} sec.$^{-1}$ which was attained after *ca.* 2% reaction and probably reflected approach to a steady-state concentration of benzhydryl bromide produced by capture of a reactive intermediate by bromide ion. The initial first-order specific rate constants, k_0, obtained are recorded in Table I, each value representing the average of at least two kinetic runs involving different solvent batches and possessing an average deviation of 1–3% with the exception of the value with perchloric acid as the added salt, for which the average deviation is 8%.

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Anomalous Infrared Absorption Frequencies Produced by Steric Effects

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We wish to report a large frequency shift of a C—H absorption frequency in some fused ring systems. In these compounds, the rings are so fused as to force two or more methylene groups into close proximity (see Fig. 1). One result of this type of structure is the appearance of a sharp, strong absorption band in the region 3055–2980 cm.$^{-1}$ in the spectra of these saturated compounds.

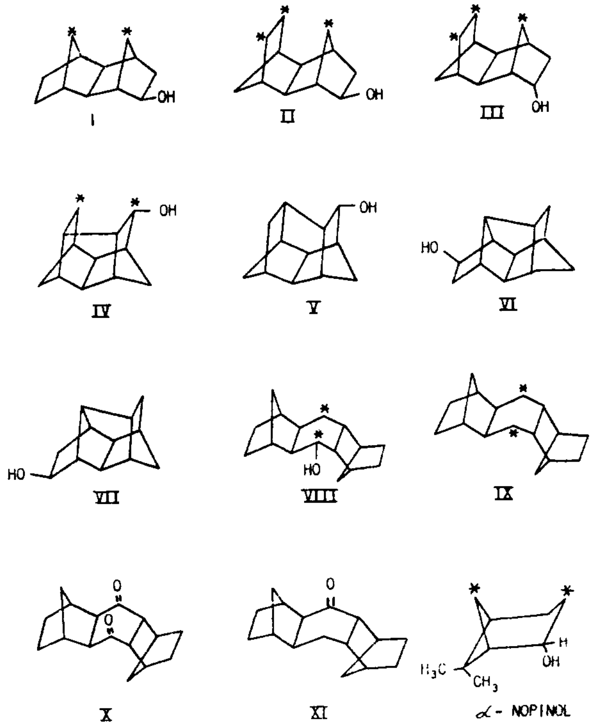

Figure 1

The frequencies and intensities of the anomalous bands are shown in Table I. The intensity data are given in terms of the integrated intensities: the observed molecular intensity in column 3, and the intensity per perturbed methylene group in column 4. No intensity data are given for compounds VIII and IX and for α-nopinol because the bands were insufficiently resolved. Compounds V, VI,

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[6] S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957).

[7] H. Sadek and R. M. Fuoss, *J. Am. Chem. Soc.*, **72**, 301 (1950).

[8] W. F. Luder, P. B. Kraus, C. A. Kraus, and R. M. Fuoss, *J. Am. Chem. Soc.*, **58**, 255 (1936).

TABLE I

ANOMALOUS FREQUENCIES AND BAND INTENSITIES

Compound	ν (cm.$^{-1}$)	$A \times 10^7$ (cm.^{2}/molecule sec.)	$A/CH_2 \times 10^7$ (cm.^{2}/group sec.)
I	3049	20.2	10.1
II	3051	11.7	3.9
III	3052	13.7	4.6
IV	3043	14.8	5.9
VIII	3018	—	—
IX	3012	—	—
α-Nopinol	2984	—	—

VII, X, and XI showed no bands in the 3055–2980 cm.$^{-1}$ region.

Typical spectra of a few of the compounds showing the anomalous band are shown in Fig. 2.

Only those compounds in Fig. 1 with starred vertices show a band in the region 3055–2980 cm^{-1}. Examination of molecular models indicates the methylene H—H distance for the starred groups is less than the H—H distance in the eclipsed form of ethane. The hydrogen atoms of the opposed methylene groups are evidently vibrating in the presence of a repulsive field, with a large component normal to the direction of vibration. Qualitatively, this would increase the frequency of vibration.

The compounds with the anomalous absorption band in the 3-μ region also show changes in the C—H bending regions of their infrared absorption spectra. These changes are not simple. Correlation of the observed spectral shifts in the bending region with changes in the molecular force fields involves consideration of more than one vibrational coordinate. The effect is well illustrated by the simple C—H stretching vibration described here.

No anomalous band appears in compounds V, VI, VII, X, and XI. The opposing C—H groups have been removed in these compounds. The ring structures have been altered, but not drastically, and it seems plausible that the anomalous band is not due to peculiarities of the ring structure. The intensities presented in Table I are comparable with normal C—H stretching mode intensities.[1] The possibility still exists that this band is one component of a Fermi resonance doublet. The wide variety of structures in which the band is observed makes this explanation improbable.

The smaller frequency changes in the cases of the rigid boat-form cyclohexane derivatives (compounds VIII and IX and α-nopinol) are of particular interest. The distances between starred vertices are somewhat greater for these compounds than those distances for the other compounds with starred vertices. A distance-frequency shift relationship would provide data on the nature of the potential between neighboring groups in molecules. Crystallographic data on these compounds would be required to determine this relationship. Dr.

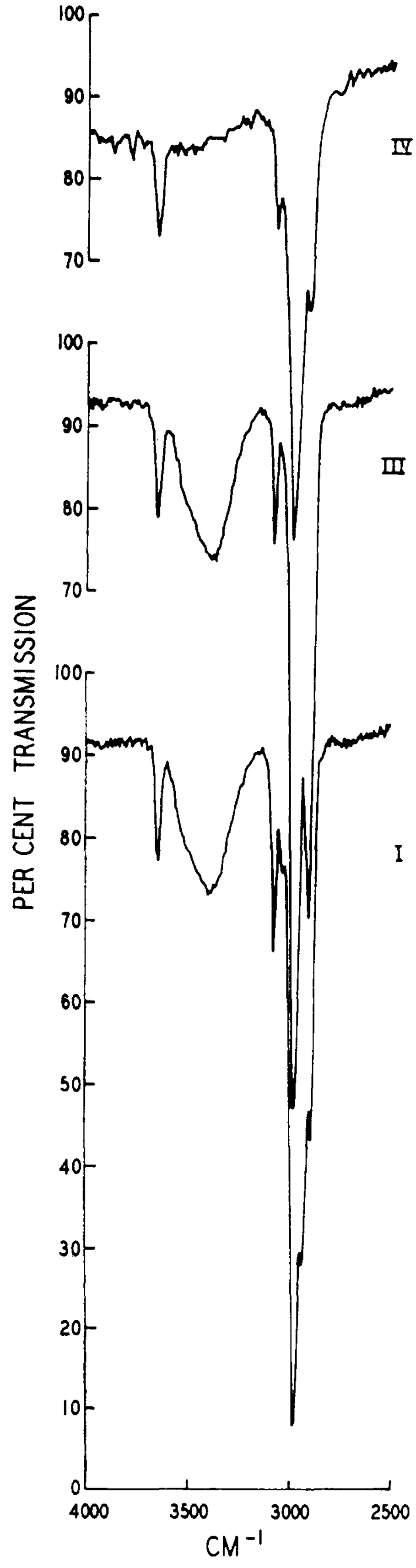

Figure 2. Typical infrared spectra of the C—H stretch region

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[1] S. A. Francis, *J. Chem. Phys.*, 18, 861 (1950).

D. G. Rea[2] has pointed out that comparative measurements of the anharmonicities of the anomalous C—H vibrations and the normal C—H vibrations would yield information on the intergroup potential function. Alternatively, if a generally applicable potential function is derived from work on barriers to hindered rotation,[3] then the distance-frequency shift relationship can be derived. Distances in rigid molecular structures could then be estimated from infrared data.

Analytically, the observation of this new band suggests the estimation of boat forms of cyclohexane derivatives in mixtures of isomers. Use of the 3050 cm.$^{-1}$ band for the identification of olefinic structures must be made cautiously in cases of complex, rigid structures.

EXPERIMENTAL

Spectrometric measurements. Preliminary survey spectra of compounds I–XI were obtained on a Perkin-Elmer Model 21, double-beam, infrared spectrophotometer with a sodium chloride prism. Quantitative spectra of compounds I–IV were obtained with a different Perkin-Elmer Model 21 infrared spectrophotometer with a lithium fluoride prism. Compounds VIII and α-nopinol were also examined in this spectrophotometer, using a calcium fluoride prism. The spectrum of compound IX in the region 3600–2500 cm.$^{-1}$ was obtained with a Beckman IR-4 spectrophotometer equipped with lithium fluoride prisms by Mr. R. Piccolini at the University of California at Los Angeles. This spectrum was made available to us by Professor S. Winstein. Cells with sodium chloride windows were used. The fused ring compounds were dissolved in carbon disulfide and the spectra of these solutions obtained in the region 3333 cm.$^{-1}$ to 2500 cm.$^{-1}$ in 0.1-mm. cells. A similar cell, filled with solvent, was placed in the reference beam.

The accuracy of the frequency calibration of the Model 21 instrument with lithium fluoride and calcium fluoride prisms was determined by observing the absorption spectrum of a polystyrene film in the C—H stretching region.[4] The frequencies in Table I are accurate to ±2 cm.$^{-1}$ For the cases where the anomalous band was sufficiently resolved, intensities were roughly evaluated using Ramsay's Method I[5] and are probably no more accurate than ±20%. This accuracy is sufficient for our purposes.

Source of compounds. α-Nopinol (m.p. 101.5–102.5°) was prepared from a sample of the acid phthalate (m.p. 128–130°) for which we are indebted to Professor S. Winstein. The structure of α-nopinol has been investigated by Winstein and Holness,[6] who conclude it is an equilibrium mixture of two isomers. The isomer with the structure shown in Fig. 1 predominates (75%).

The preparation of compound I has been described by S. B. Soloway,[7] and a sample was kindly made available to us by Julius Heiman and Company, Denver, Colo. Compounds II–VII have been briefly described by S. Winstein.[8] The details of structure assignment and preparation have been presented in a recent publication.[9] Compounds VIII and IX are derived from the diketone, X.[8,10] This diketone was converted into a monoketone, XI, by Wolff-Kishner reduction of its monoketal, followed by hydrolysis of the reduced monoketal. Lithium aluminum hydride reduction of this monoketone yields the alcohol, VIII. Dehydration of VIII followed by hydrogenation[11] yielded the hydrocarbon, IX. Details of the preparation and structure assignments of compounds VIII and IX will be presented in forthcoming publications.

Acknowledgment. We are indebted to Professor S. Winstein for suggesting that α-nopinol and the hydrocarbon IX should show the anomalous bands and for providing us with a sample of α-nopinol acid phthalate and the spectrum of IX.

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(2) D. G. Rea, private communication.

(3) E. B. Wilson, Jr., *Advances in Chemical Physics*, Vol. II, I. Prigogine (Ed.), Interscience Publishers, Inc., New York, 1959, p. 367.

(4) E. K. Plyler, L. R. Blaine, and M. Nowak, *J. Research Natl. Bur. Standards*, **58**, 195 (1957).

(5) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

(6) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 3054 (1955).

(7) S. B. Soloway, *J. Am. Chem. Soc.*, **74**, 1027 (1952).

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(11) This hydrogenation was carried out by Mr. R. Heck at the University of California at Los Angeles.

Long Range Splittings in the NMR Spectra of Isomeric 2-Bromo-2-butenes[1,2]

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The recent publication of Fraser[4] on long-range coupling between the protons in the methyl groups of tiglic and angelic acids and their methyl esters prompts us to report a similar observation in the NMR spectra of *cis*- and *trans*-2-bromo-2-butene. In this case, also, we observe coupling between the methyl group protons that are separated from one another by five bonds (four single bonds and one double bond). Furthermore, the magnitude of this coupling is larger when the two methyl groups are *trans* disposed about the olefinic linkage than when they are *cis* oriented. The possibilities of such splittings have been alluded to previously to account for the barely perceptible fine structure in one of the peaks in the NMR spectrum of methyl photosantonate.[5] Such splittings across five bonds have also been observed in the NMR spectra of

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(1) Contribution No. 2584.

(2) Supported in part by a Public Health Service Grant E-2775 from the National Institute of Allergy and Infectious Disease, U. S. Public Health Service.

(3) This investigation was carried out during the tenure of a Predoctoral Fellowship from the National Institute of Allergy and Infectious Diseases, U. S. Public Health Service.

(4) R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960).

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