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Sterically Increased C-H Stretching Frequencies in Fused Bicycloheptane and Half-cage Structures[1,2]

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Uniquely opposed methylene hydrogen atoms in certain *exo-exo*, *endo-endo* and *endo-exo* fused structures, as well as some half-cage compounds, give rise to an anomalously high C-H stretching frequency in the infrared spectrum. Structural modifications which remove the uniquely opposed hydrogen atoms cause the disappearance of this high frequency. A theory which takes account of the effect of the non-bonding interaction potential between opposing hydrogen atoms has been developed to account for the observed spectral shift. The potential is expanded in terms of the C-H stretch and the C-H-H angle, and the coupling between antisymmetric vibrations on opposing CH_2 groups is included. A simple way to estimate the degree of structural readjustment because of the opposition of methylene groups is also presented. The resulting calculations are in reasonable agreement with the experimental data.

In the investigation of the rearrangements[3,4] during solvolysis of the bromobenzenesulfonate of alcohols I and II, it was observed[4,5] that one of the four saturated alcohols which were formed, namely, the half-cage material V, displayed an anomalously high frequency band in the C-H stretching region
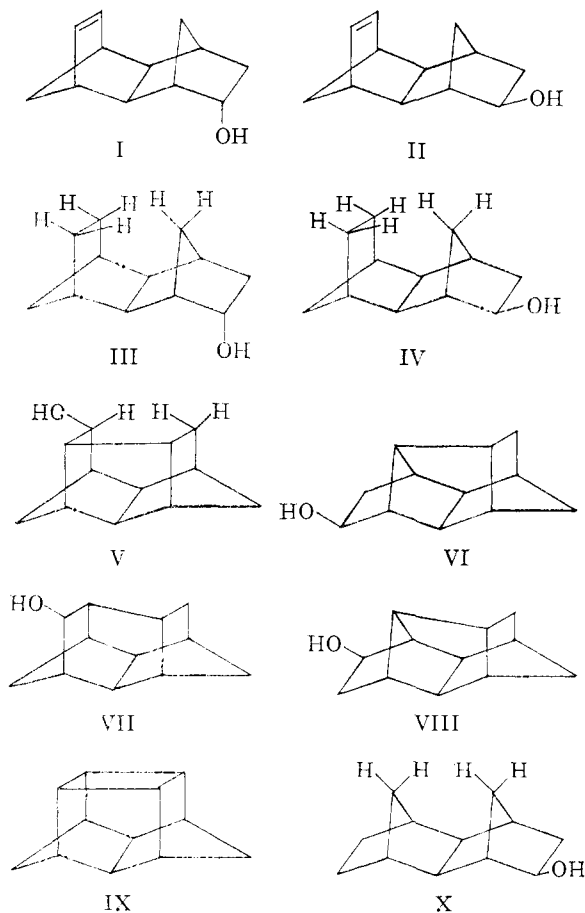
of its infrared spectrum. Such a band was absent in the spectra of the three other saturated alcohol products VI-VIII, but it was evident in the spectra of III and IV, the hydrogenation products from I and II. Further, it was not evident in the spectrum of the bird-cage hydrocarbon product IX, but it did appear for the *exo-exo* fused alcohol[6] X. The displaced high C-H stretching frequency appeared to be associated with C-H groups where large H,H interference between adjacent methylene groups exists, and its presence or absence was helpful in preliminary diagnosis of possible structures of the various observed products from I and II.[4,5]

Since the earlier work, a number of other materials have become available,[7-9] with structures related to those of I-X, and these permit us to go further in the definite correlation of the high frequency C-H stretching vibration with methylene groups which give rise to the type of hydrogen congestion indicated in III-V and X. In the present manuscript pertinent data for a substantial number of compounds are reported and discussed.

"Twisted" and *endo-exo* Fused Structures.—Of the additional compounds related to I-X which have more recently become available, some have the "twisted" carbon skeleton of alcohols VI and VIII,
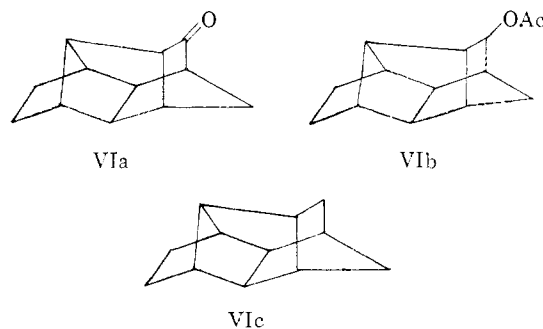
and thus they do not possess methylene groups in close proximity, such as the indicated ones in III-V and X. Consistently, they do not display an enhanced infrared C-H stretching frequency in

(1) Portions of the material in this manuscript were presented by S. Winstein at the Welch Foundation Symposium, "Molecular Structure and Chemical Change," in Houston, Tex., November 7-9, 1960.

(2) Research sponsored by the Office of Ordnance Research, U. S. Army.

(3) (a) S. Winstein, Symposium on "Dynamic Stereochemistry," Manchester, England, March 31, 1954; see *Chemistry & Industry*, 562 (1954); (b) S. Winstein *Experientia Suppl. II*, 137 (1955).

(4) L. de Vries and S. Winstein, *J. Am. Chem. Soc.*, **82**, 5363 (1960).

(5) L. de Vries, Thesis, U.C.L.A., 1956.

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

(7) (a) P. Bruck, D. Thompson and S. Winstein, *Chemistry & Industry*, 405 (1960); (b) P. Bruck, D. Thompson and S. Winstein, *ibid.*, 590 (1960).

(8) P. Bruck and D. Thompson, unpublished work.

(9) (a) S. Winstein and R. L. Hansen, *Tetrahedron Letters*, **25**, 4 (1960); (b) S. Winstein and R. L. Hansen, *J. Am. Chem. Soc.*, **82**, 6206 (1960); (c) R. L. Hansen, unpublished work.

their spectra. This is true of the "twisted" ketone[9a] VIa, acetate[9a] VIb and parent hydrocarbon[9a] VIc.

Other new compounds have the *endo-exo* fused carbon skeleton of alcohols III and IV. As is clear from Table I, which summarizes the spectra which were measured for quantitative comparison, alcohols[8,9] IVa and IVb, with a 7-OH and a 2-OH group, respectively, resemble alcohol IV closely in infrared spectrum in the C–H stretching region. All three spectra resemble that of bicycloheptane (Table I), but they show an additional sharp


IVa   IVb

IVc
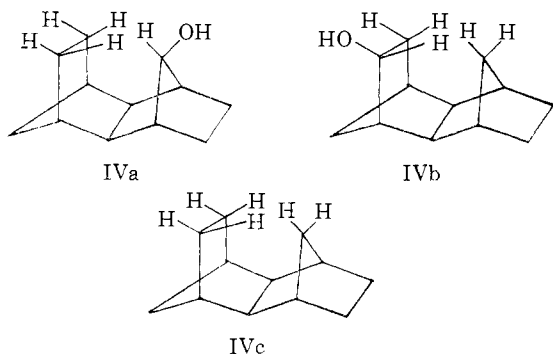
band at 3037–3049 cm.$^{-1}$, the latter being up in the range of olefinic C–H stretch, as in bicycloheptene (Table I). The same thing can be said for the parent hydrocarbon[8] IVc. Conversion of alcohol IVb to the ketone[8] IVd leaves one remaining pair of opposed methylene hydrogen atoms, and the increased C–H stretching frequency is still evident

in the spectrum of this ketone (Table I). On the other hand, conversion of alcohol IVa to ketone[9] IVe leaves no remaining opposed methylene hydrogen atoms. Consistently, ketone IVe does not have an enhanced C–H stretching frequency in its infrared spectrum.

IVd   IVe
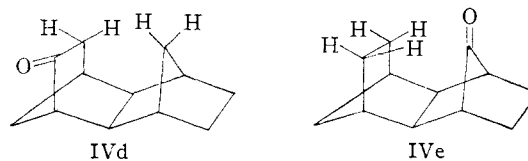
exo-exo and *endo-endo* **Fused Structures.**—As is brought out in Table I, two additional compounds with the *exo-exo* fused carbon skeleton, namely, the 7-alcohol[9] Xa and the parent hydrocarbon[9] Xb, display spectra nearly identical with that of alcohol X. All three compounds display high frequency C–H stretch at 3040–3052 cm.$^{-1}$.

Xa   Xb
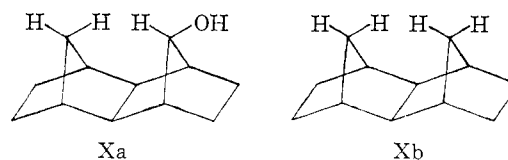
Several of the new compounds have an *endo-endo* fused carbon skeleton, and, as expected, these display high frequency C–H stretch in their infrared spectra (Table I). The compounds include alcohol[7] XIa, the parent hydrocarbon[7] XIb and the corresponding ketone[8] XIc.
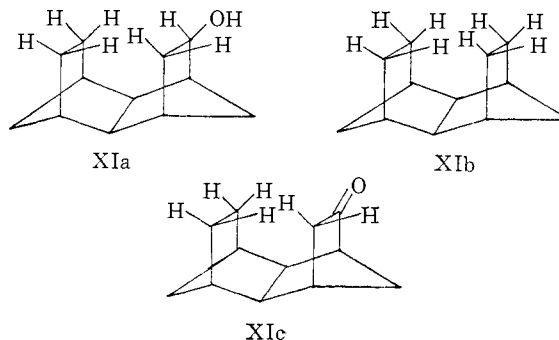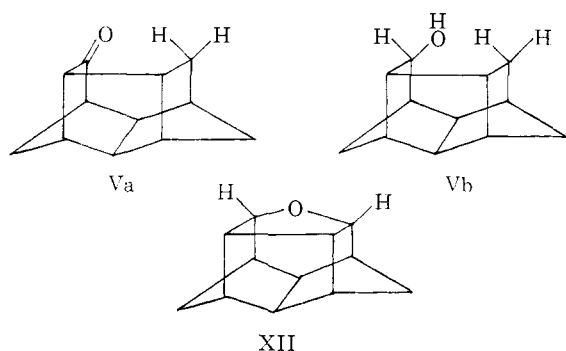


XIa   XIb

XIc

Half-cage and Cage Molecules.—The spectra of certain half-cage and cage molecules further point to the correlation of an increased C–H stretching frequency with the presence of two or more methylene hydrogen atoms in close proximity. As summarized in Table I, conversion of the half-cage alcohol V to the ketone[8] Va causes the disappearance of the high frequency band at 3048 cm.$^{-1}$. The structural change from the half-cage alcohol V to the cage oxide[8] XII also eliminates the opposed pair of hydrogen atoms from V. Consistently, the cage oxide XII does not show the enhanced C–H stretching frequency in its infrared spectrum.

The half-cage alcohol[8] Vb, epimeric with alcohol V, is interesting in the present connection. The one remaining hydrogen atom of the two opposed ones in alcohol V is now opposed by an hydroxyl oxygen atom. It may be seen from Table

TABLE I

INFRARED ABSORPTION OF VARIOUS COMPOUNDS IN THE C–H STRETCHING REGION[a]

	A	B	C	D
Cyclohexane		2934	2859	2793
Cyclodecanol	2991(sh)	2930	2868	2849
Cyclododecanol		2941	2868	2857
Bicycloheptadiene	3132	2996	2945	2877
	3119	2980		
	3077			
Bicycloheptene	3139	2974	2924	2879
	3067		2907	
Bicycloheptane		2963	2924	2879
endo-exo-Alcohol IV	3049	2955	2911	2887
endo-exo-Alcohol IVa	3037	2954	2918	2894
endo-exo-Alcohol IVb	3048	2955	2921	2879
endo-exo-Hydrocarbon IVc	3048	2953		2889
endo-exo-Ketone IVd	3039	2963	2919	2882
exo-exo-Alcohol X	3052	2959	2926	2882
exo-exo-Alcohol Xa	3040	2955	2921	2879
exo-exo-Hydrocarbon Xb	3052	2959	2930	2881
endo-endo-Alcohol XIa	3018	2960		2887
endo-endo-Hydrocarbon XIb	3031	2952		2885
				2877
endo-endo-Ketone XIc	3018	2961		2899
Half-cage alcohol V	3048	2963		2891
Half-cage ketone Va		2970	2900(sh)	2882
Half-cage alcohol Vb	3083	2961		2882
Bird-cage hydrocarbon IX		2967		2871

[a] Spectra measured on 10% solutions in carbon tetrachloride with a Beckman IR-4 spectrophotometer.

Va Vb

XII

I that a C–H stretching frequency of 3083 cm.$^{-1}$ now appears in the infrared spectrum of Vb, even more enhanced than the 3048 cm.$^{-1}$ frequency for half-cage alcohol V.

Sterically Opposed Hydrogen Atoms and Enhanced C–H Stretching Frequencies.—It seems clear that the high frequency band in the C–H stretching region observed in the spectra of the various fused bicycloheptane derivatives described above is to be ascribed to uniquely sterically opposed methylene hydrogen atoms. With respect to such opposition of certain definite hydrogen atoms, the *exo-exo*, *endo-exo* and *endo-endo* fused structures, as well as the half-cage counterparts, are certainly unique. This is clear from the approximate non-bonded H—H distances given by Dreiding scale models[10] of the various skeletons mentioned. These are

endo-endo half-cage

exo-exo endo-exo
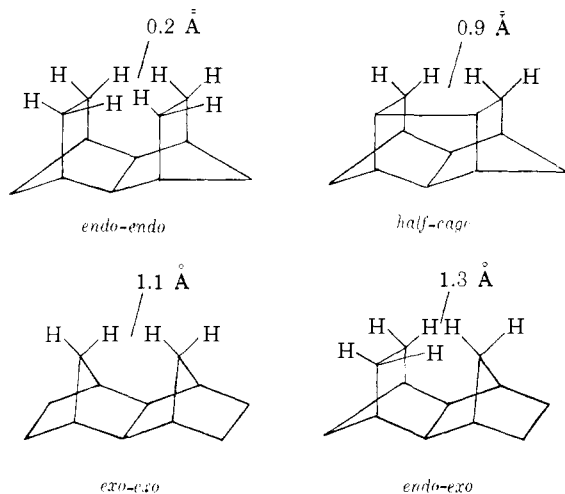
While these distances are larger in the actual molecules with compromised geometries as discussed later in this paper, it is evident that the unique non-bonded H—H distances are very far below ordinary H—H van der Waals separations.

Similarly increased C–H stretching frequencies could be expected to appear quite generally with sterically congested molecules with suitable geometry.[11] We are examining this matter further and shall comment here only on the question of the occurrence of the phenomenon in medium-sized carbocyclic rings. It is well known that such

rings are associated with relatively high energies and involve considerable hydrogen congestion.[12]

As shown in Table I, cyclodecanol does give evidence of a high C–H stretching frequency, a shoulder at 2991 cm.$^{-1}$ being present in its infrared spectrum. On the other hand, cyclododecanol, measured for comparison, does not show such an enhanced C–H stretching frequency. The presence of the enhanced C–H stretching frequency for the 10- and not the 12-ring is consistent with the greater congestion in the 10-ring than the 12. There is much chemical and physical evidence to this effect,[12] and recent structural investigations[13] show the smallest H—H distance to be above *ca.* 2.0 Å. in the 12-ring, while it is *ca.* 1.8 Å. in the 9- and 10-rings.

Assignment of Bands.—For further interpretation of the sterically increased C–H stretching frequencies in the various *endo-exo*, *exo-exo*, *endo-endo* and half-cage molecules it is necessary to make at least a partial assignment of the different observed bands. With the exception of the first few entries listed in Table I, the frequencies in columns B, C and D are clustered about 2960, 2920 and 2886 cm.$^{-1}$, respectively; these frequencies are about 30 cm.$^{-1}$ above the characteristic frequencies given by Bellamy[14] for the CH_2 asymmetric stretch, the tertiary C–H stretch and the CH_2 symmetric stretch, respectively, in unstrained molecules. These assignments also seem to be in reasonable agreement, according to the criteria of Francis,[15] with the observed intensities. A difficulty with this assignment is that the 2920 cm.$^{-1}$ line is missing in the bird-cage, *endo-endo* and half-cage molecules. However, the 2960 cm.$^{-1}$ line is unusually intense and broad in these molecules; this suggests that the *tertiary* C–H stretch has perhaps been shifted up sufficiently so as to be included in the 2960 cm.$^{-1}$ band.

The increased C–H stretching frequencies in column A of Table I represent weak lines and are thought to represent the "asymmetric" stretch of the opposed CH_2 groups; the "symmetric stretch" of these groups probably lies between 30 and 100 cm.$^{-1}$ above the entries in column D. On this basis, the difference between the frequencies in columns A and B of Table I measures the effect of the unique steric opposition in the various molecules on the C–H stretching frequency of the methylene groups involved.

Theory of Frequency Shifts.—It is possible to explain the increase of C–H stretching frequency

(10) W. Büchi Glasapparate-Fabrik, Flawil, Switzerland.

(11) See also L. de Vries and P. R. Ryason, *J. Org. Chem.*, **26**, 621 (1961).

(12) (a) V. Prelog, *J. Chem. Soc.*, 420 (1950); (b) R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1541 (1955); (c) H. C. Brown and K. Ichikawa, *Tetrahedron*, **1**, 221 (1957).

(13) E. Huber-Buser, R. F. Bryan, J. D. Dunitz, H. C. Mez and H. M. M. Shearer, page 67 of Abstracts of 5th International Congress and Symposia of International Union of Crystallography, Cambridge, England, August 15–24, 1960; see also *Helv. Chim. Acta*, **43**, 3, 18, 760 (1960).

(14) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

(15) S. A. Francis, *J. Chem. Phys.*, **18**, 861 (1950). The integrated intensity, $A = -(nL)^{-1} f \ln T d\nu$, where n = no. of molecules per cm.^{3}, L the path length, T the fraction transmission, ν the radiation frequency. For unstrained molecules $10^5 A = 1.1 N_{CH_2}, 2.7 N_{CH_2} 1.4 N_{CH}$ for the symmetrical CH_2, asymmetrical CH_2, tertiary CH stretch. repectively; N_{CH_2} and N_{CH} are the number of CH_2 and CH groups per molecule, respectively.
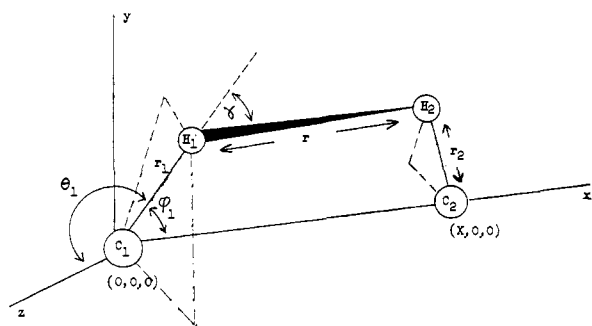
Fig. 1.—Diagram of opposed methylene hydrogen atoms.

by taking account of the non-bonded repulsion between opposed hydrogen atoms H_1 and H_2 shown schematically in Fig. 1. Because of this H---H opposition, the C—H vibration is associated with an effectively larger force constant and coupling occurs between the C—H_1 and C—H_2 stretches.

The hypothetical structure of the molecule in the absence of non-bonding interactions between the opposing hydrogens can be estimated from Dreiding models. The opposing hydrogens are often absurdly close according to this model, *i.e.*, 0.2Å. for the *endo-endo* structure, and we must, therefore, consider the effect of a non-bonding potential energy ϕ upon the structure. If this potential energy and all the molecular force constants are known, a more realistic "equilibrium structure" can be obtained by minimizing the total energy of the molecule. In practice this cannot be done and the "equilibrium structure" must usually be obtained by direct measurements, *i.e.*, X-ray diffraction data. However, in the absence of good structural information an approximate calculation, as outlined above, can be carried out; such a procedure is illustrated in the last section of this article.

Let us assume that the "equilibrium structure" is known and let the H---H distance r have the equilibrium value r_e (see Fig. 1). Since stretching frequencies are much larger than torsional ones, it will be assumed that the distance r_e as well as the "equilibrium bond angles" can, in principle, be determined without altering bond lengths and stretching frequencies from their values in molecules free from non-bonding interactions. However, the effect of the non-bonding potential ϕ upon the C–H bonds must be considered in the "equilibrium structure." To do so one assumes that the potential ϕ is a function of the distance between non-bonding centers only; in our case we will assume that the non-bonding interaction takes place entirely between opposing hydrogens. The nature of the potential $\phi(r)$ and the validity of the approximations introduced is discussed in the next section.

The total potential energy of the molecule can be expanded about the "equilibrium structure." We are interested only in the C–H stretching motions in opposing CH_2 groups, and since these vibrations are nearly independent of the other molecular motions we will consider only terms in the potential energy that depend solely upon variations in the C–H bond lengths on the opposing
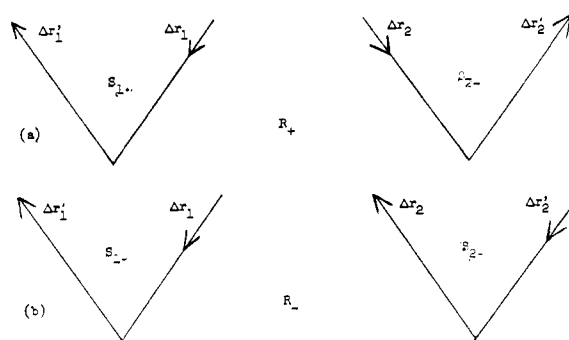

Fig. 2.—Coupled asymmetric stretching modes: (a), symmetric–asymmetric mode; (b), asymmetric–asymmetric mode.

methylene groups. In the absence of the non-bonding potential the contribution to the energy from C–H stretches is U_0 as given in eq. 1. In this

$$U_0 = (1/2)k_0(\Delta r_1{}^2 + \Delta r_1{}'^2 + \Delta r_2{}^2 + \Delta r_2{}'^2) +$$
$$k_{11}{}'(\Delta r_1 \Delta r_1{}' + \Delta r_2 \Delta r_2{}') \quad (1)$$

equation Δr_1 and $\Delta r_1{}'$ represent the variations in length of the C–H bond on one of the methylene groups; the unprimed symbol refers to the C–H bond directly opposed to the other methylene group (see Fig. 2); Δr_2 and $\Delta r_2{}'$ are analogous quantities referred to the other methylene group; k_0 and $k_{11}{}'$ are the unstrained force constants for C–H stretching on methylene groups. To U_0 we must add the contribution from the expansion of $\phi(r)$. The terms in $\Delta r_1{}'$ and $\Delta r_2{}'$ that arise in this expansion of $\phi(r)$ are omitted because they contribute to the vibrational frequencies only in second order.[16] The significant contribution to the stretching energy from the non-bonding interactions is given in eq. 2.

$$\phi(\Delta r_1, \Delta r_2) = \sum_{i=1}^{2} (k - k_0)[\Delta r_i +$$
$$(\partial \phi\{r_e\}/\partial r)k_0{}^{-1} \cos \gamma]^2/2 + k_{12}\Delta r_1 \Delta r_2 \quad (2)$$

In this equation the new force constants k and k_{12} are given in eq. 3 and 4. In order to obtain eq.

$$k = k_0 + (\partial^2 \phi\{r_e\}/\partial r^2) \cos^2 \gamma + r_e{}^{-1} (\partial \phi\{r_e\}/\partial r) \sin^2 \gamma \quad (3)$$

$$k_{12} = (\partial^2 \phi\{r_e\}/\partial r^2) \cos^2 \gamma - r_e{}^{-1} (\partial \phi\{r_e\}/\partial r) \sin^2 \gamma \quad (4)$$

2 the derivatives $\partial r/\partial r_i$ and $\partial^2 r/\partial r_i{}^2$ that appear in the expansion of $\phi(r)$ have been evaluated with the aid of Fig. 1. Equation 2 describes the change in stretching force constants $(k - k_0)$ and the coupling of the stretching motions of the two methylene groups (k_{12}) as well as the shift in the C–H equilibrium distance. The latter is small and will be neglected.

The vibrational frequencies can best be calculated by introducing a coördinate transformation. An asymmetric stretch S_{1-} and a symmetric stretch S_{1+} can be introduced for the first methylene group: $S_{1\pm}$ is given in eq. 5. Analogous asym-

$$S_{1\pm} = 2^{-1/2}(\Delta r_1 \pm \Delta r_1{}') \quad (5)$$

metric and symmetric stretches $S_{2\pm}$ can be defined for the other methylene group. U_0 is completely separable in these four new coördinates;

(16) Modify the equations given by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp. 148, 149, 169.

however, these coördinates are coupled in the $\phi(\Delta r_1, \Delta r_2)$ contributions to the energy. All cross terms between symmetric S_+ and asymmetric S_- terms can be neglected since these cross terms contribute to the asymmetric vibrations only in second order. Cross terms in S_1-S_2- are important, however, since the S_1- and S_2- modes are degenerate in the absence of these cross terms. The potential energy for the asymmetric vibrations is thus nearly separable from that for other motions; it can be obtained by adding $\phi(\Delta r_1, \Delta r_2)$ to U_0, carrying out the coördinate transformation described above, dropping all terms containing S_{1+} or S_{2+}, and introducing two new coördinates: the "symmetric–asymmetric" stretch R_+ and the "asymmetric–asymmetric" stretch R_- defined in eq. 6 (see Fig. 2). The asymmetric stretching

$$R_\pm = 2^{-1/2}(S_{1-} \pm S_{2-}) \qquad (6)$$

potential U is then given in eq. 7. It is seen that

$$U = (k + k_0 - 2k_{11}' + k_{12})R_+{}^2/4 +$$
$$(k + k_0 - 2k_{11}' - k_{12})R_-{}^2/4 \quad (7)$$

the two asymmetric stretching modes are separable and that two well defined stretching frequencies $\bar\nu_+$ and $\bar\nu_-$, corresponding to R_+ and R_-, respectively, will result. If $\bar\nu_0$ is the asymmetric vibration characteristic of molecules without nonbonding interactions ($\bar\nu_0 \approx 2960$ cm.$^{-1}$), c the speed of light, M the hydrogen mass, α the H–C–H angle in the CH_2 group ($\alpha \approx 109°$), then the frequency shifts in wave numbers are given by eq. 8.

$$\Delta\bar\nu_\pm = \bar\nu_\pm - \bar\nu_0 = (k - k_0 \pm k_{12}) \times$$
$$[1 + (1/_6) \sin^2 \alpha]/32\pi^2 \bar\nu_0 Mc^2 \quad (8)$$

In obtaining this equation the condition $\bar\nu_0 \gg |\bar\nu_\pm - \bar\nu_0|$ has been applied.

Equation 8 along with the auxiliary eq. 3 and 4 depend upon the assumptions that a non-bonding interaction potential $\phi(r)$ exists, that it can be meaningfully expanded to second order about the "equilibrium structure" and that a number of interaction terms can be discarded in the potential energy. Only the first of these assumptions need be pursued. Non-bonding intramolecular potentials are notoriously ineffective in explaining effects such as hindered internal rotation: however, in the molecules under study the interacting hydrogens are four saturated carbon–carbon bonds apart which guarantees that the interaction is "non-bonding" and rather more like an intermolecular interaction for which potentials of the form $\phi(r)$ have been devised successfully.

Unless γ is very close to 90° (see Fig. 1), the shift in the "symmetric–asymmetric" mode $\Delta\bar\nu_+$ is very much greater than the shift in the "asymmetric–asymmetric" mode $\Delta\bar\nu_-$. One would also expect $\bar\nu_-$ to be more intense than the former; this agrees with the observed fact that the $\bar\nu_+$ lines recorded in column A of Table I are weak and shifted quite far from $\bar\nu_0$ while the $\bar\nu_-$ lines recorded in column B are not shifted appreciably and are roughly as intense as they would be were there no $\bar\nu_+$ shifted out to higher frequency. The $\bar\nu_+$ has a finite transition probability only because the separation of symmetric S_+ and asymmetric S_- modes is not complete. In the limit that this mixing vanishes, the intensity of $\bar\nu_+$ vanishes and

$\bar\nu_-$ has an intensity equal to the sum of the intensities of the two uncoupled asymmetric modes S_{1-} and S_{2-}. The theory is compatible with weak S_+S_- mixing and the observed spectra.

The effect of non-bonding interactions upon the symmetric stretches (2885 cm.$^{-1}$) is complicated and will not be considered here. It should be noted that all twists of one CH_2 plane relative to the other have been neglected.

Estimation of Frequency Shifts.—In order to evaluate the frequency shift, an expression for the potential $\phi(r)$ must be assumed. No thoroughly satisfactory potential has been proposed, but a Buckingham[17] (exp., 6) potential is most often employed. The potential in eq. 9, where c.g.s. units are used throughout, will be chosen for the present work. The coefficient of the r^{-6} term is

$$\phi(r) = 12.7 \times 10^{-10} [\exp - (4.98 \times 10^8 r)] -$$
$$3.42 \times 10^{-60} r^{-6} \quad (9)$$

that suggested by Pitzer and Catalano[18]; the potential minimum has been fixed at 2.35 Å., the distance reported by Kitaygorodsky.[19] Also the value of $(\partial\phi/\partial r)$ at 1.36 Å. was adjusted to that used by Bartell[20] who in turn based it upon spectroscopic data.[21]

By means of the potential 9, it is possible to calculate the frequency difference $\bar\nu_+ - \bar\nu_-$ as a function of the H_1---H_2 distance r_e and the angle γ between the C---H_1 bond and the H_1---H_2 line. When γ is small the non-bonding force is directed almost entirely along the C–H bond and, therefore, has a maximum effect on the frequency shifts; when γ is large the force has only a small component along the C–H bond. The results of the calculations are summarized in Table II by listing the values of the angle α compatible with various values of r_e for frequency differences $\bar\nu_+ - \bar\nu_-$ equal to 95 and 79 cm.$^{-1}$. The asymmetric–asymmetric shifts $\Delta\bar\nu_-$ corresponding to given values of r_e and γ are also given in Table II.

TABLE II

ANGLES γ $(\bar\nu_+ - \bar\nu_-)$ AND FREQUENCY SHIFTS $\alpha\bar\nu_-(\bar\nu_+ - \bar\nu_-)$ AS FUNCTIONS OF $\bar\nu_+ - \bar\nu_-$ AND r_e

r_e, Å.	γ values (degrees)		$\Delta\bar\nu_-$, cm.$^{-1}$	
	γ (95)	γ (79)	$\Delta\bar\nu_-$ (95)	$\Delta\bar\nu_-$ (79)
1.30	71	77	−56	−60
1.40	57	63	−26	−28
1.45	50	56	−15	−18
1.50	41	48	−18	−11
1.55	29	39	−4	−6
1.60	3	25	0	−2

The use of other potential functions does not alter the qualitative picture. A more exact description would include interactions other than the H_1---H_2 one. The general equations derived in the previous section are, of course, more valid the better the potential function used.

(17) Hirschfelder, Curtiss and Bird, "Molecular Theory of Gases and Liquids," J. Wiley and Sons, Inc., New York, N. Y., 1954, p. 180.

(18) K. S. Pitzer and E. Catalano, J. Am. Chem. Soc., 78, 4844 (1956).

(19) A. F. Kitaygorodsky, Tetrahedron, 9, 183 (1960).

(20) L. S. Bartell, J. Chem. Phys., 32, 827 (1960).

(21) R. S. Mulliken, J. Am. Chem. Soc., 72, 4493 (1950); 77, 887 (1955).

The H_1---H_2 distance and the angle between the C—H bond and the H_1---H_2 line given by Dreiding scale models of the half-cage, exo-exo (Xb) and endo-endo (XIb) hydrocarbons are listed in Table III as r_0 and γ_0 values. Also listed are the observed frequency differences $\bar{\nu}_+ - \bar{\nu}_-$. The frequency difference for the half-cage hydrocarbon is

TABLE III
STRUCTURE AND FREQUENCY DIFFERENCES AND SHIFTS IN SEVERAL MOLECULES

	Half-cage	exo-exo-Xb	endo-endo-XIb
r_0, Å.: models	0.91	1.08	0.2
γ_0, deg.: models	48	39	27
$\bar{\nu}_+ - \bar{\nu}_-$, cm.$^{-1}$: exptl.	99	93	79
r_e, Å.: calcd.	1.52	1.52	1.40
γ_e, deg.: calcd.	69	58	70
$\gamma_e{}^*$, deg.: Table II	35	39	63
$\Delta\bar{\nu}_-$, cm.$^{-1}$: Table II	−6	−6	−28

not known, but it is estimated at about 14 cm.$^{-1}$ greater than that for the half-cage alcohol V. This estimate is made on the basis of a comparison between the exo-exo (Xb) and endo-endo (XIb) hydrocarbons with their corresponding alcohols Xa and XIa. It is clear from Table II that much larger $\bar{\nu}_+ - \bar{\nu}_-$ values would be expected if the actual r_e and γ_e values were equal to the listed r_0 and γ_0 figures. Obviously, these $\bar{\nu}_+ - \bar{\nu}_-$ differences have been reduced by the changes in r and γ in the actual equilibrium molecules.

Although at the present time we do not know the "equilibrium structure," if the potential function used is adequate, with the aid of Table II we can put some limits on r_e and γ_e. We note that if r_e is 1.3 Å., or even 1.4 Å., the shift $\Delta\bar{\nu}_-$ to low frequency of the asymmetric–asymmetric line is very large. An analysis of Table I indicates that such a shift probably is not more than 10 cm.$^{-1}$; according to Table II this requires an r_e distance greater than 1.45 Å. for the three molecules discussed in the preceding paragraph and in Table III. Furthermore, since the equilibrium value of γ_0, γ_e, is larger than the value γ_0 obtained from Dreiding models, we can with the aid of Table II and the γ_0 values given in Table III obtain upper limits for r_e; these are approximately 1.45, 1.50 and 1.58 Å. for the half-cage exo-exo hydrocarbon (Xb) and endo-endo hydrocarbon (XIb), respectively. When r_e distances are obtained experimentally these limits can be checked, and the comparison used to improve the potential function.

Estimation of Structure.—The calculations in this section are offered only as a means of estimating the applicability of the above calculations and should not reflect upon the results in the previous sections which will be tested more critically when structures are known more accurately. However, these calculations should temporarily help to knit together the preceding theory.

It is virtually impossible to calculate the equilibrium structure because the torsional force constants are not known. However, one may obtain some idea of the structural adjustment resulting from the presence of the non-bonding interactions by assuming that all angles but the $H-C_1-C_2$

angle ϕ_1 and its C_1-C_2-H counterpart ϕ_2 are unchanged (cf. Fig. 1). The rigid molecules under consideration are subject to strain which will resist the torsional distortion of the carbon skeleton; this suggests that the C–C–C angles can be held fixed in a first approximation. This is a rather poor approximation but it will yield an upper limit to the value of γ assuming that the potential function is correct. Also, the H_1—H_2 distance r does not depend as critically upon θ_1 and θ_2 (cf. Fig. 1) as upon φ_1 and φ_2 and this implies that the distortion of φ_1 should be much greater than that of θ_1. The dependence of the energy upon φ_1 and φ_2 in the hypothetical structures given by the Dreiding models is assumed to be of the form given in eq. 10.

$$U'(\varphi) = f[(\varphi_1 - \varphi_1{}^0)^2 + (\varphi_2 - \varphi_2{}^0)^2]/2 \qquad (10)$$

where f is a torsional force constant and φ^0 is the equilibrium value of φ in the absence of non-bonding forces. Of course, eq. 10 is valid only for small variations of angle, but we shall assume that it holds for large changes. In molecules for which $\theta_1 = \theta_2 = \pi/2$ (cf. Fig. 1), φ_1 is equal to γ. Adding $\phi(r)$ to $U(\varphi)$ and minimizing with respect to φ_1 and φ_2, we arrive at eq. 11 for γ_e, the equilibrium value of γ.[22]

$$\gamma_e - \gamma_0 = \frac{\sin \gamma_e \, r_1{}^{-1}}{(fr_1{}^{-2})} \, \partial\phi(r_e)/\partial r_e \qquad (11)$$

With the aid of eq. 11, r_e and γ_e values may be estimated for the half-cage, exo-exo (Xb) and endo-endo (XIb) hydrocarbons, and these are listed in Table III. These r_e and γ_e figures are substantially larger than the r_0 and γ_0 values from the Dreiding scale models and considerably more reasonable, especially for the endo-endo hydrocarbon XIb. Reference to Tables II and III shows that the r_e and γ_e values come much closer to accounting for the $\bar{\nu}_+ - \bar{\nu}_-$ frequency shifts and the lack of $\bar{\nu}_- - \bar{\nu}_0$ shifts than do the r_0 and γ_0 counterparts. In Table III a comparison is shown between the γ_e values and those angles $\gamma_e{}^*$ compatible with the calculated r_e and observed $\bar{\nu}_+ - \bar{\nu}_-$ differences on the basis of Table II. In all cases the value obtained for γ_e is larger than the value $\gamma_e{}^*$; this indicates that the carbon skeleton alters and takes up much of the strain imposed by the non-bonding potential. At this point it is not worthwhile to carry out elaborate calculations on the structural changes but rather to try to obtain good structural data experimentally. While the spectral shifts are not fitted quantitatively, they are sufficiently well accounted for that one can have reasonable confidence in the over-all description presented. In spite of the many approximations implicit in the whole treatment, it is certainly helpful in understanding the high C–H stretching frequencies encountered with the unique molecules described.

It should be pointed out that although $r_0 = 0.2$ Å. for the endo-endo molecule we do not require that $\phi(r)$ give a description for such small r's since $\partial\phi/\partial r$ in eq. 11 is evaluated at r_e. However, it is also true that r_e appears to be considerably less than the 2.35 Å. equilibrium distance selected for the potential in eq. 9.

(22) $fr_1{}^{-2}$ can be taken as 0.46×10^5 dynes cm.$^{-1}$, the value for angle bending in methane and r_1 is ca. 1.1 Å.; see ref. 16, p. 182.

Experimental Part

Materials.—Most of the compounds employed for the spectral measurements were either described elsewhere[4,6,7,9] or else available from other investigations in progress.[8,9] We are indebted to Dr. S. B. Soloway of the Shell Development Co. for the *exo-exo* fused alcohol[6] X and to Dr. J. Abell of the California Research Corp. for a sample of cyclododecanol. Also, we are grateful to Professor Prelog of the E.T.H., Zurich, Switzerland, who kindly made a sample of cyclodecanol available to us through Dr. Richard

Heck, and to Professor Robert L. Scott for some useful comments concerning the theory.

Spectral Measurements.—Measurements in the C–H stretching region were carried out on 10% solutions in carbon tetrachloride with a Beckman IR-4 spectrophotometer equipped with lithium fluoride optics. Observed frequencies were corrected by means of a calibration of the instrument with a polystyrene film.[23]

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

Tetrasubstituted Cyclooctatetraenes: Catalytic Cyclotetramerization of Propiolic Acid Esters With Tetrakis-(phosphorus trihalide)-Nickel(0) Complexes[1]

BY JOSEPH R. LETO AND MARILYN F. LETO

Cyclotetramerization of methyl or ethyl propiolate to form positional isomers of tetracarbomethoxy- or tetracarbethoxy-cyclooctatetraene is catalyzed in hydrocarbon solvents by tetrakis-(phosphorus trihalide–nickel(0) complexes. 1,2,4,6- and 1,3,5,7-substitution on the cyclooctatetraene ring was established mainly from proton magnetic resonance spectra. Partial hydrogenation of the 1,2,4,6-isomers yields the cyclooct-7-enes, whereas total hydrogenation of the 1,2,4,6- and 1,3,5,-7-isomers yields the cyclooctanes. Saponification of cyclooctatetraene-, cyclooctene- and cyclooctane-carboxyesters yields the corresponding acids. This type of catalysis has been attempted using a wide variety of other unsaturated monomers and other zero valent complexes, but has been found to be extremely limited in scope. The reaction provides, however, a useful route to a rare class of compounds.

Introduction

The carbonyls of iron, cobalt and nickel, as well as many of their organic and inorganic derivatives, have proved to be quite active as polymerization catalysts for acetylenic compounds. However, the catalytic activity of a particular metal carbonyl derivative for polymerizing a given monomer is sometimes remarkably specific. This report describes a further example of such specific catalytic activity and the novel products obtained.

Reppe[2] has discussed the cyclotrimerization of monosubstituted acetylenes in the presence of zero valent nickel-carbonyl-phosphine catalysts to give trisubstituted aromatic products. With the catalyst $Ni(CO)_2[P(C_6H_5)_3]_2$, for example, propargyl alcohol was cyclized to a mixture of 1,2,4- and 1,3,5 - trimethylolbenzene. Similarly, the highly reactive ethyl ester of propiolic acid undergoes aromatization[3] to give a mixture of 1,2,4-

$$3RC{\equiv}CH \xrightarrow{Ni(CO)_2(P(C_6H_5)_3)_2}$$

and 1,3,5-tricarbethoxybenzene. In most cases the unsymmetrical isomer is favored. The nature of these cyclizations with nickel-carbonyl-phosphine catalysts has been under investigation in this Laboratory. It has been found[4a,4b] that catalyst activation in these trimerizations most probably

(1) Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

(2) J. W. Reppe and W. J. Schweckendiek, *Ann.*, **560**, 104 (1948).

(3) L. S. Meriwether, E. C. Colthup, G. W. Kennerly and R. N. Reusch, *J. Org. Chem.*, in press.

(4) (a) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 1200 (1959); (b) L. S. Meriwether, E. C. Colthup, M. L. Fiene, G. W. Kennerly and R. N. Reusch, Abstracts of Papers, 138th Meeting, American Chemical Society, New York, N. Y., September, 1960, p. 67-P.

proceeds by way of a tricoördinated nickel(0) species, and that the dissociation of carbon monoxide followed by coördination of an acetylene molecule is responsible for catalytic activity. Whether or not this activity requires the presence

$$Ni(CO)_2(PR_3)_2 \rightleftharpoons [Ni(CO)(PR_3)_2] + CO$$
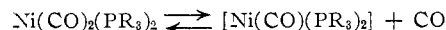
of CO ligand(s) in the original nickel complex is uncertain.

The CO-free tetrakis-(phosphorus trihalide)-nickel(0) complexes, $Ni(PX_3)_4$ (X = F, Cl, Br), have now been investigated as catalytic initiators for acetylene cyclizations. Preliminary P^{31} nuclear magnetic resonance (n.m.r.) studies of phosphine exchange in these complexes in solution indicate that one or more of the phosphine ligands is subject to a reversible dissociation producing a ligand-

$$Ni(PX_3)_4 \rightleftharpoons [Ni(PX_3)_n] + (4-n)PX_3$$
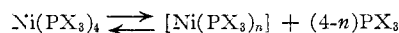
deficient nickel(0) species containing only phosphines. The ability of these tetrakis complexes to catalyze the formation of novel cyclic products has been demonstrated in this work.

Results and Discussion

Cyclization Reactions.—We have found that in the presence of each of the three different tetrakis-(phosphorus trihalide)-nickel(0) compounds mentioned above, as well as the tetrakis-(phenyldichlorophosphine) analog, cyclization of ethyl propiolate proceeds in a fashion different from the trimerization reactions, forming a mixture of stable tetramers in addition to the aromatic trimers. These tetramers have been identified as 1,2,4,6- and 1,3,5,7-tetracarbethoxycyclooctatetraene (I and II). The reaction is carried out at room temperature under a blanket of nitrogen by adding $Ni(PCl_3)_4$ in cyclohexane or benzene to $HC{\equiv}CCOO-C_2H_5$ in the same solvent. Under these conditions the temperature rises 50–60°, and 73% of the