[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Vibrational Energy Level Splitting and Optical Isomerism in Pyramidal Molecules of the Type XY_3[1]

BY RALPH E. WESTON, JR.

RECEIVED JANUARY 14, 1954

The vibrational energy level splittings and rates of racemization have been estimated for several pyramidal molecules with N, P, As, Sb and S as central atoms. The calculations are based on a potential energy function which is derived from known vibrational frequencies and molecular dimensions. It is concluded that energy level splittings for all molecules but ammonia are too small for observation, and that optically active compounds of arsenic, antimony and sulfur should be stable toward racemization at room temperature.

Introduction

The existence of a double potential energy minimum in the configuration of pyramidal molecules leads, at one extreme of energy barrier height, to a splitting of vibrational levels observable in the infrared and microwave regions; at the other extreme it is related to the phenomenon of optical activity.

Vibration Energy Level Splitting.—The potential energy for a pyramidal molecule XY_3 (Fig. 1a) is a function similar to that of Fig. 1b, in which x is the distance of the X atom from the plane of the Y atoms. The vibrational eigenfunction for the molecule can then be formed from a suitable combination of the eigenfunctions which would be obtained for the separate regions about x_0 and $-x_0$ if $V(x)$ did not have the finite value $V_{\max}$ in the region $-x_0 < x < x_0$. The unperturbed case is represented by the dotted line in Fig. 1b. The problem is formally analogous to that of the hydrogen molecule-ion.[2] Using the variation method, one finds that each unperturbed vibrational level is now split into a symmetric and an anti-symmetric level, and these are separated by $\Delta E = 2\int_{-\infty}^{+\infty} \psi(x_0)\, H\psi(-x_0)\mathrm{d}x$, where H is the usual vibrational Hamiltonian operator and the ψ's are the unperturbed vibrational eigenfunctions. With rather arbitrarily chosen potential functions, this method has been applied to the ammonia molecule.[3]

A different approach was used by Dennison and Uhlenbeck,[4] who applied the Wentzel–Kramers–Brillouin approximation method to the general problem, and found the energy level splitting for the nth vibrational level to be given by

$$\Delta E_n = h\nu_2/\pi \exp\left\{(4\pi/h)\int_0^{x_1} [2m(V - E_n)]^{1/2}\mathrm{d}x\right\} \qquad (1)$$

where ν_2 is the frequency of the symmetrical deformation vibration,[5] x_1 is the lower value of x at which $V(x) = E_n = (n + {}^1/_2)h\nu_2$, and $m = 3m_Y/[1 + (3m_Y/m_X)]$ is the reduced mass for this vibrational mode. For ammonia, this method gives energy level splittings in better agreement with the observed values than does the variation method, if the same potential function is used in both methods.

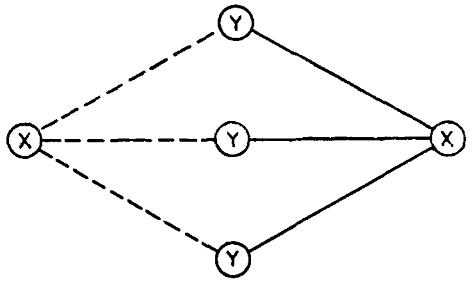


Fig. 1a.—Equilibrium configurations of XY_3 molecule.

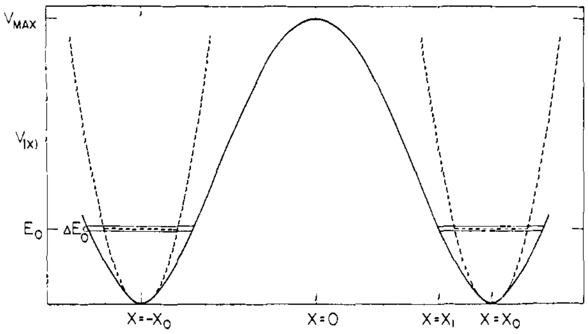


Fig. 1b.—Vibrational potential function for XY_3 molecule of Fig. 1a; dotted line, unperturbed case with infinitely high inversion barrier; solid line, perturbed case with inversion barrier height $V_{\max}$.

Slightly different methods have been used by Manning,[6] by Rosen and Morse,[6] and by Newton and Thomas.[6] However, in all the methods mentioned above, the form of the potential function was not calculable independent of a knowledge of the energy level splitting. A common procedure was to use the observed splitting of the first vibrational level to fix parameters and to then calculate the splitting of higher levels, or of different isotopic species. In a recent paper, Costain and Sutherland[7] have derived the potential from vibrational force constants and molecular parameters alone. The inversion is assumed to take place by a gradual increase in the amplitude of the symmetrical deformation vibration ν_2, until the molecule passes through the planar configuration with $x = 0$. Using a valence force model for the vibrational potential, the potential function is given by

$$V = (3/2)\{k_1(\Delta l)^2 + k_\delta(\Delta\alpha)^2\} \qquad (2)$$

---

[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 192 ff.

[3] P. M. Morse and E. C. G. Stueckelberg, *Helv. Phys. Acta*, **4**, 337 (1931); F. T. Wall and G. Glockler, *J. Chem. Phys.*, **5**, 314 (1937).

[4] D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.*, **41**, 313 (1932).

[5] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 110.

[6] M. F. Manning, *J. Chem. Phys.*, **3**, 136 (1935); N. Rosen and P. M. Morse, *Phys. Rev.*, **42**, 210 (1932); R. R. Newton and L. H. Thomas, *J. Chem. Phys.*, **16**, 310 (1948).

[7] C. C. Costain and G. B. B. M. Sutherland, *J. Phys. Chem.*, **56**, 321 (1952).

where k_1 is the usual X–Y bond-stretching force constant, k_δ the bond-bending force constant, and Δl and $\Delta\alpha$ are the changes in bond length and interbond angle from the equilibrium values. The inversion barrier height is $V_{\max} = V(\alpha)\ (120° - \alpha)/57.3°$, where α is the equilibrium interbond angle.

The extension to deformations of about 20° in the interbond angle of force constants derived from vibrations which are assumed harmonic is certainly open to question. However, when the potential function calculated in this way is combined with the approximation method of Dennison and Uhlenbeck, the energy level splittings calculated for ammonia are in excellent agreement with the observed values.

Stereochemistry of Pyramidal Molecules.—When the time-dependence of the vibrational eigenfunction for an XY_3 molecule is considered, it is found that the probability density is a maximum alternately for the X atom at $x = x_0$ and at $x = -x_0$; the frequency of this alternation in probability density is $f_n = 2\Delta E_n/h$, where ΔE_n, as before, is the vibrational energy level splitting.[8] If the three Y atoms or groups are different, two alternate positions of the X atom obviously lead to molecules which are enantiomorphs, and hence such a molecule should possess optical activity.[9] The interconversion of the two forms (racemization) is a particular type of unimolecular reaction, and there are the usual two routes by which this may take place.

(1) Quantum mechanical tunneling through the potential energy barrier, which occurs with a rate constant given by

$$k_t = \frac{\sum\limits_n \exp[-h\nu_2(n + {}^1/_2)/kT]\Delta E_n}{h\sum\limits_n \exp[-h\nu_2(n + {}^1/_2)/kT]} \qquad (3)$$

which is calculable from equation 1. If the reduced mass and barrier area are sufficiently small, this may be the more rapid process.

(2) Passage over the barrier, the rate of which can be calculated from absolute reaction rate theory. According to this, the rate constant for a unimolecular reaction is given by[10]

$$k_1 = \kappa\,\frac{\sigma_r}{\sigma\ddagger}\left(\frac{A\ddagger B\ddagger C\ddagger}{A_rB_rC_r}\right)\frac{\prod\limits^{3n-7}(1 - e^{-h\nu\ddagger/kT})^{-1}}{\prod\limits^{3n-6}(1 - e^{-h\nu_r/kT})^{-1}} \times \frac{kT}{h} \times e^{-E_0/RT} \qquad (4)$$

where κ is the transmission coefficient (which can be calculated in principle from the potential function, but will be assumed equal to unity), σ is the symmetry number, A, B and C are principal moments of inertia, the products are terms involving vibrational frequencies, and the subscripts r and ‡ refer to the reactant molecule and the activated complex. E_0 is the energy difference between the lowest level of the reactant molecule and that of the activated complex, and is approximately our $V_{\max}$ (Fig. 1b). For the approximation used in this paper, it is safe to assume that the terms preceding kT/h are of the order of unity. In the temperature region considered, $kT/h \simeq 10^{12} - 10^{13}$ sec.$^{-1}$.

By calculating rates of tunneling through and passage over the barrier, one can make an estimate of the stability toward racemization of a particular molecule. This was done for several molecules by Kincaid and Henriques,[9b] who used the potential function $V = 4\pi^2\nu_2^2m(/x/ - /x_0/)^2$ suggested by Wall and Glockler.[3]

The purpose of this paper is to report similar calculations using more recent values of molecular dimensions and vibrational frequencies, and using potentials calculated according to the method of Costain and Sutherland.[7] The method consists of calculating bond-stretching and bond-bending force constants from the observed frequencies ν_1 and ν_2.[11] (In most cases force constants were also calculated from ν_3 and ν_4 as a check.) Equation 2 can be rewritten in the form $V(\alpha) = (3l^2/2)\ [k_1(\Delta l/l\Delta\alpha)^2 + (k_\delta/l^2)]\ (\Delta\alpha)^2 = K(\Delta\alpha)^2$ and K is then calculated from the force constants and molecular parameters relating Δl and $l\Delta\alpha$. Using the relationship $\cos\alpha = [(3x^2/l^2) - 1]/2$, one obtains $V(x)$ from $V(\alpha)$, and a plot is made of $V(x)$ against x. Graphical integration is then used to evaluate equation 1, with the assumption that the reduced mass is independent of x. The unimolecular rate of passage over the barrier, $k_1 \equiv 10^{13}e^{-V_{\max}/RT}$, is given in terms of a "racemization temperature" T_r, the temperature at which the half-time for racemization is two hours.

The necessary data and the results of these calculations are given in Table I and in the following discussion. It may be pointed out that in general quite different values for the inversion barrier are found than were found by Kincaid and Henriques.

Results and Discussion

Nitrogen as the Central Atom.—The values in Table I for ammonia are those given by Costain and Sutherland.[7] Their calculations were repeated as a check on these values. The calculated energy level splittings are $\Delta E_0 = 0.789$ cm.$^{-1}$ and $\Delta E_1 = 36.6$ cm.$^{-1}$, compared with observed values of 0.7935[12] and 35.8 cm.$^{-1}$.[13] The excellent agreement between calculated and observed values indicates the usefulness of the method. A rough calculation for ammonia using the observed fundamentals, instead of the frequencies corrected for anharmonicity gave $\Delta E_0 = 0.811$ cm.$^{-1}$, still in good agreement with experiment.

A similar set of calculations for ammonia-d_3 leads to values which are in not quite as good agreement with observed values: $\Delta E_0 = 0.0782$ and $\Delta E_1 = 6.57$ cm.$^{-1}$ compared with observed values of 0.0532 (microwave spectrum)[14] and 3.4 (infrared spectrum)[13] or 3.9 (microwave spectrum) cm.$^{-1}$.[15] The

---

(8) Reference 2, p. 310.

(9) (a) An excellent qualitative discussion of this in terms of quantum mechanical principles is given by W. Kuhn in "Stereochemie," Vol. 1, ed. K. Freudenberg, Franz Deuticke, Leipzig, 1933, pp. 390–394. (b) J. F. Kincaid and F. C. Henriques, Jr., THIS JOURNAL, **62**, 1474 (1940).

(10) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 191.

(11) Reference 5, p. 175.

(12) B. Bleaney and R. P. Penrose, *Nature*, **157**, 339 (1946).

(13) D. M. Dennison, *Rev. Mod. Phys.*, **12**, 175 (1940).

(14) R. G. Nuckolls, L. J. Rueger and H. Lyons, *Phys. Rev.*, **89**, 1101 (1953).

(15) J. H. N. Loubser and J. A. Klein, *ibid.*, **78**, 348A (1950).

TABLE I

Compound	X–Y, Å.	α	ν_1	ν_2	k_1	k_δ/l^2	$V(\alpha)$, kcal./mole-rad^2	V_{max}, kcal./mole
			cm.$^{-1}$		10^5 dynes/cm.			
NH_3	1.014[a]	106°46′[a]	3539[b]	1055[b]	7.21	0.474	111	5.93
ND_3	1.014[a]	106°46′[a]	2524[b]	803[b]	7.11	.478	106	5.67
ND_3	1.014	106°46′	2524	803	7.21	.474	117	6.22
$N(CH_3)_3$	1.47[c]	109°[d]	827[e]	365[e]	4.12	.398	222	8.19
PH_3	1.415[f]	93°18′[f]	2323[g]	991[g]	3.11	.292	126	27.4
PH_3	1.415[f]	93°18′[f]	2460[h]	1070[h]	3.49	.340	147	31.8
$P(CH_3)_3$	1.87[c]	100°[c]	653[i]	263[i]	2.78	.214	180	22.0
PF_3	1.55[j]	104°[j]	892[k]	487[k]	6.21	.984	578	45.1
PCl_3	2.04[l]	100°[l]	510[m]	257[m]	2.43	.440	558	68.1
PBr_3	2.18[c]	100°5′[c]	400[n]	116[n]	1.67	.213	455	52.7
AsH_3	1.523[o]	91°30′[o]	2209[o]	974[o]	2.86	.282	141	35.0
$As(CH_3)_3$	2.05[c]	96°[c]	568[i]	223[i]	2.44	.182	166	29.2
$Sb(CH_3)_3$	2.15[p]	96°[q]	513[i]	188[i]	2.12	.142	152	26.7
$S^+(CH_3)_3$	1.82[r]	109°5′[s]	654[t]	285[t]	3.16	.357	487	16.5
$S^+(CH_3)_3$	1.82[r]	100°[u]	654[t]	285[t]	2.80	.256	198	24.1

[a] Reference 5, p. 439. [b] Corrected for anharmonicity; ref. 13. [c] P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950). [d] R. Spitzer and K. S. Pitzer, THIS JOURNAL, **70**, 1261 (1948), quoting V. Schomaker, private communication. [e] K. W. F. Kohlrausch, *Monatsh.*, **68**, 349 (1936). [f] Average of values for PH_2D and PHD_2; M. H. Sirvetz and R. E. Weston, Jr., *J. Chem. Phys.*, 21, 898 (1953). [g] V. M. McConaghie and H. H. Nielson, *Proc. Natl. Acad. Sci. U. S.*, **34**, 455 (1948). [h] With estimated correction for anharmonicity. [i] E. J. Rosenbaum, D. J. Rubin and C. R. Sandberg, *J. Chem. Phys.*, **8**, 366 (1940). [j] O. R. Gilliam, H. D. Edwards and W. Gordy, *Phys. Rev.*, **75**, 1014 (1949). [k] M. K. Wilson and S. R. Polo, *J. Chem. Phys.*, **20**, 1716 (1952). [l] P. Kisliuk and C. H. Townes, *Phys. Rev.*, **78**, 347 (A) (1950). [m] D. M. Yost and T. F. Anderson, *J. Chem. Phys.*, **2**, 624 (1934). [n] ν_3 and ν_4 used rather than ν_1 and ν_2, since the latter lead to complex values of force constants. J. Cabannes and A. Rousset, *Ann. phys.*, **19**, 229 (1933). [o] Dimensions recalculated from moments of inertia; frequencies corrected for anharmonicity. V. M. McConaghie and H. H. Nielsen, *Phys. Rev.*, **75**, 633 (1949). [p] Calculated from covalent bond radii of M. L. Huggins, THIS JOURNAL, **75**, 4126 (1953). [q] By comparison with values for $SbCl_3$ and $As(CH_3)_3$ in ref. c. [r] By comparison with values for $(C_2H_5)_2S$ and $(CH_3)_2S$ in ref. c. [s] By comparison of X-ray crystal structures for $[(CH_3)_3S]_2SnCl_6$ and $[(CH_3)_3NH]_2SnCl_6$; R. B. Corey and R. W. G. Wyckoff, *Radiology*, **15**, 241 (1930). [t] H. Siebert, *Z. anorg. allgem. Chem.*, **271**, 65 (1952); assignment of frequencies by comparison with $P(CH_3)_3$. [u] By comparison with $P(CH_3)_3$.

difference in force constants for the two isotopic species is an indication of the error in the valence-force approximation; this in turn produces a difference in the inversion barrier height. A calculation for ammonia-d_3 using the force constants for ammonia leads to $\Delta E_0 = 0.0395$ and $\Delta E_1 = 4.41$ cm.$^{-1}$.

It must be emphasized that an error of a few per cent. in the calculation of the barrier area leads to a much larger absolute error (amounting to orders of magnitude) in the tunneling rate for heavy molecules than it does for ammonia. This follows from the sensitive exponential relation between energy-level splitting and the square of the barrier area. The unimolecular rate constants are slightly less sensitive, since they depend exponentially on the barrier height.

For trimethylamine (and the other trimethyl compounds) calculations were made treating the methyl group as a single mass concentrated at the center of mass of the group. For trimethylamine, the rate constant for tunneling from the lowest energy level is 7.4 sec.$^{-1}$, and the "racemization temperature" is 105°K., so that tunneling would be the more important racemization process. The corresponding energy level splitting is 3.7 cycles/sec., which is not in a spectroscopically accessible region.

Unfortunately, no suitable data are available for higher molecular weight amines. The situation is complicated by the similarity in carbon and nitrogen masses and the similarity of force constants for carbon–carbon and carbon–nitrogen bonds. Thus it is no longer a reasonable approximation to treat the molecule as a sytem of four masses. For the specific case of triethylamine, the interbond angle is 4° greater than that of trimethylamine,[16] but at the same time the pyramid height is increased slightly. The reduced mass increases by a factor of almost two, but the relative increase is less for higher members of the homologous series. A consideration of structural models indicates that the activated complex with a plane of symmetry perpendicular to the threefold axis can only be formed when the methyl groups have rotated about the carbon–carbon bond, or the C–C–N angle has increased to 180°. The rotation is sterically hindered, and the bending process would have a high energy barrier. In consideration of the above factors it is reasonable to assume that higher molecular weight amines would have an inversion barrier similar to that for trimethylamine, in which case optical isomers could not be separated even at low temperatures. Despite a very large amount of experimental work,[17] no optically active trivalent nitrogen compound has been found.

Phosphorus as the Central Atom.—Calculations made by Costein and Sutherland for phosphine were repeated, and a considerably different result was obtained. (This was principally due to their use of molecular parameters which have been more accurately determined recently.) The value obtained for ΔE_0 is 10^{-3} cycle/sec., which is far beneath any present method of observation. A rough estimate was made of the anharmonicity correction to ν_1 and ν_2 (from the known corrections for NH_3

---

(16) Reference *d*, Table 1.

(17) R. L. Shriner, R. Adams and C. S. Marvel, Chapter IV of "Organic Chemistry, an Advanced Treatise," ed. H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943.

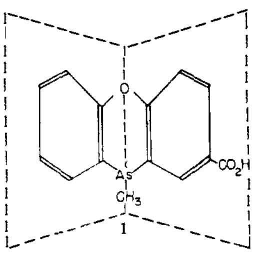
and AsH_3), and the second set of calculations led to $\Delta E_0 = 10^{-7}$ cycle/sec. This demonstrates how sensitive the inversion frequency is to a slight change in force constants. In all cases, however, the force constants corrected for anharmonicity will be larger, so that the calculated barrier heights are lower than they should be.

The calculations for trimethylphosphine are entirely analogous to those for trimethylamine, and lead to a value of $T_r = 280$°K. The tunneling rate is of the same order of magnitude as the unimolecular rate. If the temperature is lowered to 200°K., both rate constants are reduced to 10^{-11} sec.$^{-1}$. If other trivalent phosphorus compounds have similar inversion barriers, it is evident why no optical activity in such compounds has been observed (despite considerable experimental work), since the half-time for racemization at room temperature is about an hour. However, it should be possible to prepare such compounds if the necessary chemistry can be done at a low temperature.

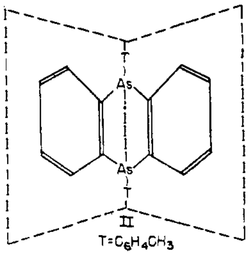
The phosphorus trihalides all have inversion barriers of similar height. From these one obtains the following values of T_r: PF_3, 580°K.; PCl_3, 880°K.; PBr_3, 680°K. The tunneling rate will be much less than that for trimethylphosphine because of the larger reduced mass and higher barrier. The possibility of preparing and resolving trihalides of the type $PX_1X_2X_3$ does not appear very encouraging, however, since mixed trihalides decompose to the simple trihalides in a period of days.[18]

Arsenic as the Central Atom.—The calculations made by Costain and Sutherland for arsine were repeated, and the only difference noted was a value of 0.282×10^5 dynes/cm. for k_δ/l^2 compared to their value of 0.258×10^5. This increases the barrier height slightly and the value for ΔF_0 becomes 2.6×10^{-18} cm.$^{-1}$ or 7.8×10^{-8} cycle/sec.

For trimethylarsine, the value of T_r is 380°K. (at which temperature the tunneling rate is one-tenth the unimolecular rate), indicating the possibility of resolving trivalent arsenic compounds. Indeed, this has been reported for 10-methylphenoxarsine-2-carboxylic acid (I) and 5,10-di-*p*-tolyl-5,10-dihydroarsanthrene (II).[19] In the case of I, the C–O–C bond angle must be distorted in the process of obtaining a planar configuration about the arsenic atom, and this will lead to a higher inversion barrier than that calculated for trimethylarsine. A similar consideration applies to inversion about either arsenic atom of II.



I



II

T=$C_6H_4CH_3$

Optical isomers of compounds of the type $[AsR_1R_2R_3R_4^+]X^-$ have also been resolved, but the inversion process here is analogous to that with carbon rather than a trivalent atom as the asymmetric central atom.

Antimony as the Central Atom.—Trimethylstibine has a racemization temperature of 340°K. and the tunneling rate is even lower than that for trimethylarsine. Hence asymmetric trivalent antimony compounds should exist as resolvable optical isomers.

Sulfur as the Central Atom.—The results obtained for the trimethylsulfonium ion are rather surprising. Unfortunately, the interbond angle in such compounds has not been determined experimentally. Two assumed angles were used for calculations: the tetrahedral angle, by analogy with the ammonium ion, and 100°, by analogy with trimethylphosphine, which is isoelectronic with the trimethylsulfonium ion. In the first case, the calculated inversion barrier is rather low, leading to $T_r = 210$°, and $k_1 = 10$ sec.$^{-1}$ at 298°K. The second choice of angle gives $T_r = 310$°K., $k_1 = 3 \times 10^{-5}$ sec.$^{-1}$, and a tunneling rate constant of this same order of magnitude. These latter values are very close to those for trimethylphosphine. Experimentally, however, asymmetric sulfonium salts have been resolved and are quite stable to racemization.[20] Thus the calculated barrier height is too low, even with the second choice of angle. This, of course, is in agreement with the earlier statement that the use of force constants not corrected for vibrational anharmonicity leads to low barrier heights.

In conclusion, the calculations reported here lead to the following predictions: (1) no molecule except ammonia with a trivalent Group V element as the central atom has a vibrational energy level splitting which is within orders of magnitude of the region covered by current spectroscopic techniques, (2) it is very improbable that optical isomers of trivalent nitrogen compounds can be found, even at very low temperatures, (3) it should be possible to obtain optically active trivalent phosphorus compounds if the chemistry can be done at low temperatures, while similar compounds of arsenic and antimony should be stable to racemization at room temperature and above.

UPTON, LONG ISLAND, NEW YORK

---

[18] H. S. Booth and S. G. Frary, THIS JOURNAL, **61**, 2934 (1939).

[19] Reference 17, p. 429 ff.

[20] Reference 17, p. 419.