

Absolute Configuration of Optically Active Molecules

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out very closely, as opposed to hydrogen-deuterium isotopic pairs where the observed frequency ratio is generally a few percent smaller than the mass term.

In other cases the spectra of the two species permit a calculation of the three force constants in the most general quadratic potential function

$$2V = f_1 \Delta r_1^2 + f_2 \Delta r_2^2 + 2f_{12} \Delta r_1 \Delta r_2.$$

However, it was found that no *significant* value for the interaction term, f_{12} , could be calculated for ClCN. The isotopic shifts are not sensitive to the value of f_{12} in this case. The values of the principle force constants which reproduce the observed frequencies as shown in Table I are given in Table II. The frequencies are recalculated from the average values.

TABLE II. Force constants for ClC¹³N and ClC¹⁵N ($f_{12}=0$) in units of 10^8 dynes/cm.

	From ClC ¹³ N	From ClC ¹⁵ N	Average
$f_1(\text{C}-\text{Cl})$	4.931	4.926	4.928
$f_2(\text{C}=\text{N})$	17.03	17.00	17.01

While it was not possible to calculate an exact value for f_{12} , calculations indicate that it is small and probably positive. A value for f_{12} of 1×10^8 dynes/cm probably represents a reasonable upper limit consistent with possible errors in the frequency measurements. Values of the principle force constants consistent with various values of f_{12} between 0 and 1×10^8 dynes/cm were calculated. It was found that f_1 varied between 4.7 and 5.0×10^8 dynes/cm and f_2 varied between 16.8 and 18.2×10^8 dynes/cm. These probably represent reasonable limits to the true values of f_1 and f_2 in the observed frequency approximation. The value of 4.9×10^8 dynes/cm for the carbon-chlorine force constant represents a considerable stiffening over the "normal" value. This is almost certainly due to resonance of the pure covalent structure with the double-bonded chlorine structure $\text{Cl}=\text{C}=\text{N}$, and if the latter structure is important, we should expect a positive value for the interaction term.

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Mass Spectra of N₂¹⁴, N¹⁴N¹⁵ and N₂¹⁵

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November 23, 1949

WE have recently had an opportunity to analyze a sample of nitrogen gas from Eastman Kodak Company containing approximately 65 atom percent N¹⁵. The mass spectrum of this material permits an accurate calculation of the relative amounts of doubly charged N₂⁺⁺ ions and a calculation of the dissociation patterns of the three isotopic nitrogen molecules.

The mass spectra were obtained with a model 21-102 Consolidated mass spectrometer using conventional techniques. The temperature of the ionization chamber was about 245°C.

The doubly charged ion at $m/e=14.5$ has an intensity relative to the 29⁺ ion of zero for 20 v electrons, 0.99 percent for 50 v, 2.62 percent for 70 v, and 3.78 percent for 100 v electrons. Table I summarizes the calculations and the mass spectra for 50 v electrons. Columns 1 and 2, respectively, give the mass and relative abundance of all ions observed in the mixture spectrum. The peak at $m/e=14.5$ is entirely (N¹⁴N¹⁵)⁺⁺. The contributions of the isotopic ions, (N₂¹⁴)⁺⁺ and (N₂¹⁵)⁺⁺ to $m/e=14$ and 15 are computed by multiplying the intensity of the 14.5 peak by the ratios 26.3/100 and 94.6/100. The resulting values appear in column 3.

TABLE I. Mass spectra of N₂¹⁴, N¹⁴N¹⁵ and N₂¹⁵ for 50 v electrons.

m/e	Mixture pattern	Doubly charged ions	Singly charged ions			Patterns	
			N ₂ ¹⁴	N ¹⁴ N ¹⁵	N ₂ ¹⁵	N ₂ ¹⁴	N ₂ ¹⁵
14	5.36	0.26	1.77	3.33		6.73	
14.5	0.99	0.99					
15	10.0	0.94		3.33	5.73		6.06
28	26.3		26.3			100	
29	100			100			
30	94.6				94.6		100

The contribution to $m/e=14$ of the singly charged ion (N¹⁴)⁺ from N₂¹⁴ can be computed from the 28 peak by correcting the $m/e=14$ pattern coefficient of normal nitrogen obtained under identical conditions for a 1 percent contribution from the doubly charged molecule ion as determined above. The contributions of N₂¹⁴ appear in column 4. The remaining contribution at $m/e=14$ is from the (N¹⁴)⁺ dissociation of N¹⁴N¹⁵. Equal probability of formation of the (N¹⁵)⁺ ion from N¹⁴N¹⁵ is now assumed. This is reasonable since Friedel and Sharkey¹ have shown H⁺ and D⁺ from HD to be of nearly equal probability. Thus, the dissociation pattern of N¹⁴N¹⁵ is given in column 5. The remaining contribution to $m/e=15$ is due to the (N¹⁵)⁺ dissociation of N₂¹⁵ and is given in column 6. The normalized dissociation patterns of N₂¹⁴ and N₂¹⁵ corrected for doubly charged ions are given in columns 7 and 8.

A significant difference in the dissociation probability of N₂¹⁴ and N₂¹⁵ is observed. This is undoubtedly of the same origin as that observed for H₂ and D₂.^{2,3} A similar effect is to be expected in the dissociation of C¹²O₂ and C¹³O₂. This would result in ambiguity in the observed isotopic abundance if for some reason the abundance is measured for a dissociated ion rather than the molecule ion. We are at present investigating this possibility.

¹ R. A. Friedel and A. G. Sharkey, Jr., J. Chem. Phys. 17, 584 (1949).

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³ D. P. Stevenson, J. Chem. Phys. 15, 409 (1947).

Absolute Configuration of Optically Active Molecules

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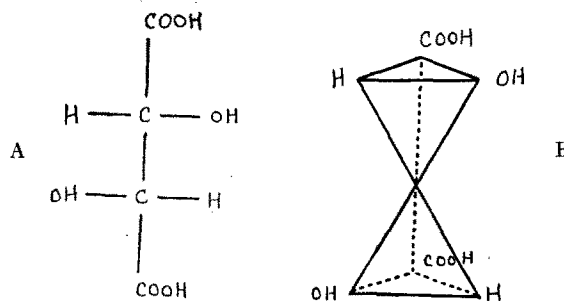
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November 18, 1949

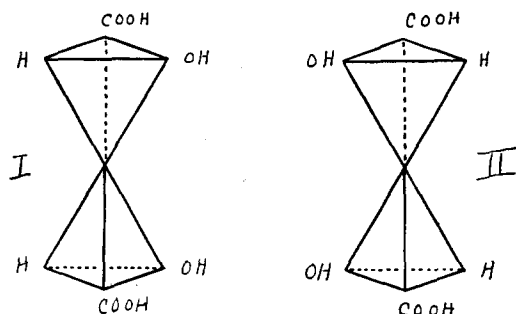
FOLLOWING Fischer, the usual convention¹ is that the molecule of *d*-tartaric acid shall be written as the "projection formula" A, this implying that particular disposition B of the spatial



configuration in which for convenience one-half of the molecule has been rotated about the main axis in order to bring the two carboxyl groups below the plane of the paper and the two hydrogen atoms and the two hydroxyl groups into that plane. This

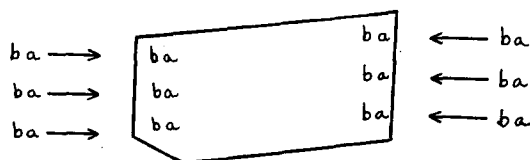
process does not imply hindrance of free rotation within the molecular configuration, insofar as tartaric acid in solution is concerned, and does not predicate any particular disposition within the molecular configuration which might have to be adopted in order that from molecules the crystal could be built.

The recent preliminary analysis of the crystal structure of *d*-tartaric acid² in fact indicates that in the crystalline state, if (in any one molecule) the two hydrogen atoms and the two hydroxyl groups are all in, or approximately in, the same plane (e.g. that of the paper), then one carboxyl group is above and the other below that plane, the planes of the acid groups themselves being steeply inclined the one to the other. The two possibilities for the molecule in the crystal are thus the enantiomorphic configurations:



Between these, x-ray methods cannot distinguish.

Recently, however, J. Waser³ has claimed that it is possible to make the distinction if crystal structure is considered in relation to crystal habit; that is, in relation to growth. He argues that, given the structure determined by Beevers and Stern,² the known habit of *d*-tartaric acid crystals would only be formed for molecules of the type II and that the Fischer convention is therefore incorrect. His argument is based on an examination of the ease with which hydrogen bonds may form, and persist, in various directions at the crystal surface as new molecules are deposited. He suggests, in fact, that a polar crystal grows differently at opposite ends simply because if the molecules themselves are asymmetric, *ab*, then the ease of attachment of an *a* end to a *b* face



will be different from that of a *b* end to an *a* face, and that it is possible to judge which event is the more likely.

Now we question very strongly whether such a judgment is possible on the basis of bond formation alone, and we do not think, therefore, that Waser's conclusion is valid. There is no *a priori* reason why the attachment *ba*→*ba* should form more readily than that of *ab*→*ab*. The bond is mutual.

Nevertheless it is true that polar crystals *do* often grow differently at the opposite ends of the uniterminal axis, and various causes may contribute to this otherwise curious phenomenon.

It may be that a face *b* is more easily "poisoned" than a face *a*, possibly by the occasional attachment of solvent molecules *c*.⁴ Or again the solvent molecules may form temporary attachments more readily with the *a* end than with the *b* end of the "free" molecule and prevent its adherence to the crystal surface. But it would surely be much more difficult to put forward any convincing argument for the probability of a particular habit formation in an actual case on this kind of basis, and yet that, it seems, is what would be required for a determination of absolute configuration by such means.

At present, therefore, there is no sound evidence either for or against the correctness of the Fischer convention.

¹ Freudenberg, *Stereochemie*, p. 662-3; Werner, *Lehrbuch der Stereochemie*, p. 31, 92.

² Beevers and Stern, *Nature* **162**, 854 (1948).

³ Jürg Waser, *J. Chem. Phys.* **17**, 498 (1949).

⁴ Wells, *Crystal Growth* (Gurney and Jackson, London, 1949), Faraday Society Discussion No. 5, p. 200.

Isomer Distribution in Fischer-Tropsch Hydrocarbons

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November 10, 1949

A STATISTICAL derivation of the isomer distribution observed in Fischer-Tropsch products has recently been given.¹ This derivation involved the implicit assumption that the various isomers of a given molecular weight cut add carbon atoms (to form the next higher molecular weight cut) in proportion to their concentrations. Dr. R. B. Anderson has pointed out² that the calculation can also be made on the basis of the assumption that the isomers of a given cut add carbon atoms in proportion to the number of (weighted) ways that addition can occur to the individual isomers. The rules for addition given in reference 1 may be maintained unchanged. This may be illustrated by a particular example: The distribution of *C*₄ isomers is unchanged; that of *n*-butane remains $2a/(a+1)$ and that of *i*-butane, $b/(a+1)$. *N*-butane can react to form *n*-pentane in $2a[2a/(a+1)] = 4a^2/(a+1)$ ways, or to form *i*-pentane in $2b[2a/(a+1)] = 4ab/(a+1)$ ways; *i*-butane can react to form *i*-pentane in $3a[b^2/(a+1)] = 3ab/(a+1)$ ways. The total number of (weighted) ways in which all of the *C*₄ isomers can react is $(4a^2+7ab)/(a+1)$, of which $4a^2/(a+1)$ give *n*-pentane and $7ab/(a+1)$ give *i*-pentane. The fraction of *n*-pentane in the *C*₅ cut is, therefore, $4a^2/(4a^2+7ab) = 4a/(4+3b)$, and the fraction of $7ab/(4a^2+7ab) = 7b/(4+3b)$.

Extension of the calculation to the remaining molecular weight fractions leads to the data of Table I. The table is simplified in the sense that the computation has been made only for those isomers experimentally observed; this does not materially affect the results. It is clear that use of this alternate basis of calculation

TABLE I. Alternate calculation of isomer distributions.

Isomer	Formula	Mole percent in cut	
		Calculated (<i>a</i> = 0.975, <i>b</i> = 0.025)	Observed
<i>n</i> -pentane	$\frac{4a}{4+3b}$	0.957	0.950
<i>i</i> -pentane	$\frac{7b}{4+3b}$.043	.050
<i>n</i> -hexane	$\frac{8a}{8+21b}$.911	.896
2-methyl pentane	$\frac{15b}{8+21b}$.044	.057
3-methyl pentane	$\frac{14b}{8+21b}$.041	.047
<i>n</i> -pentane	$\frac{16a}{16+73b}$.876	.877
2-methyl hexane	$\frac{31b}{16+73b}$.043	.046
3-methyl hexane	$\frac{58b}{16+73b}$.081	.077
<i>n</i> -octane	$\frac{32a}{32+209b}$.838	.845
2-methyl heptane	$\frac{63b}{32+209b}$.042	.039
3-methyl heptane	$\frac{120b}{32+209b}$.081	.072
4-methyl heptane	$\frac{58b}{32+209b}$.039	.044