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## Errata: A Relation between Bond Order and Covalent Bond Distance **FREE**


H. J. Bernstein





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
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Warrick who have kindly supplied us with samples of the trimethyl silicon chloride.

Our best thanks are due Professor C. A. Coulson and to Dr. D. M. Simpson who have read the manuscript and kindly revised the English.

<sup>1</sup> R. L. Livingston and L. O. Brockway, *J. Am. Chem. Soc.* **68**, 719 (1946).

<sup>2</sup> C. A. Coulson, *V. Henri Memorial Volume* (Deseer, Liège, 1947); C. A. Coulson, J. Duchesne, and C. Manneback, *ibid.*; A. D. Walsh, *Trans. Faraday Soc.*, meeting on free radicals (in the press); J. Duchesne, *Nature* **159**, 62 (1947).

<sup>3</sup> N. Wright and M. J. Hunter, *J. Am. Chem. Soc.* **69**, 803 (1947).

<sup>4</sup> F. T. Wall and C. R. Eddy, *J. Chem. Phys.* **6**, 107 (1938).

### Errata: A Relation between Bond Order and Covalent Bond Distance

[*J. Chem. Phys.* **15**, 284 (1947)]

H. J. BERNSTEIN

National Research Council, Ottawa, Canada

IN the table for CN, CO, and NO bonds, the bond orders are 0, 1, and 2 for single, double, and triple bonds instead of 1, 2, and 3 as in the table; the C≡O distance is 1.11 instead of 1.15.

### Errata: "Volume Effect" and Random Flights

[*J. Chem. Phys.* **16**, 839 (1948)]

R. C. BRIANT

Mellon Institute, Pittsburgh, Pennsylvania

IN a previous Letter to the Editor the proposed solution is wrong, in part, because the definition of "loop" is ambiguous. Also, multiple loop configurations are over-weighted. The writer regrets the error.

### A Note on the Structure of Insulin\*

DOROTHY WRINCH

Department of Physics, Smith College, Northampton, Massachusetts

August 16, 1948

A COMPREHENSIVE x-ray study of a "wet" insulin crystal has been carried out by Dr. Crowfoot and her collaborators. Much of the work is at present unpublished because of the war. A preliminary publication gave the

space group  $R3$ , cell dimensions  $a=83.0\text{\AA}$ ,  $c=34.0\text{\AA}$ , and the Patterson projection on the basal plane.<sup>1</sup> A report to the Rockefeller Foundation in 1942 by Dr. Crowfoot included her calculation of the basal section of the Patterson-Harker map and calculations by Dr. K. Schiff of lines parallel to the trigonal axis, including those extending over a  $5A$  region about it and an estimate of molecular weight 36,000. A general account based on this report appeared in Russian in 1946.<sup>2</sup> Dr. Crowfoot has generously given me a list of the intensities recorded. We are very greatly indebted to Dr. W. J. Eckert and the International Business Machine Corporation for making available the facilities of the Watson Scientific Computing Laboratory, to Dr. L. H. Thomas for planning, and to Miss E. A. Stewart for carrying out the calculation of the complete three-dimensional Patterson-Harker map derived from these intensities, for  $z$  in thirtieths, and for  $x$  and  $y$  in sixtieths.

Figure 1 shows sections from this map parallel to the basal plane, in the neighborhood of the trigonal axis. The following features may be remarked: a *positive* region  $A$  enclosing the origin with circumscribing sphere of radius  $8.2A$ ; a *negative* region  $B$  completely inclosing  $A$ ; and a *positive* region  $C$  extending slightly further than from  $z=\frac{1}{2}\pm\frac{1}{6}$ . Since the full extent of the insulin structure or of any molecule in it cannot be represented by so small a region as  $A$ , the region  $B$  suggests the presence of a lower electron density distribution within each molecule, i.e., a cage structure for each molecule comprising a closely integrated space-enclosing atomic fabric. Structures of this morphological type<sup>3</sup> were suggested for protein molecules in 1936. These include the  $C_1$  cage which, it is now seen,<sup>4</sup> can comprise 72 to 48 residues per skeleton, the  $C_2, \dots, C_n, \dots$  cages with maximum skeletal residue numbers 288,  $\dots, 72n, 2 \dots$ .

A possible picture of the insulin structure is thus as follows: each particle comprises  $m$  trigonal molecules ( $m=0, 1, \dots$ ) and  $n$  triads of molecules not necessarily trigonal ( $n=0, 1, \dots$ ), each being a cage structure. Oncley's recent finding<sup>5</sup> that the insulin structure ( $MW\sim 36,000$ ) may be dissociated into 3 subunits suggests that  $m=0$ , leaving  $n$ , the number of molecules per subunit, to be determined.

These new data, so far as suggestions of the "cage" type are concerned, thus appear to favor the suggestion of an insulin structure made up of  $C_1$  cages<sup>6</sup>—say 6—or of 3

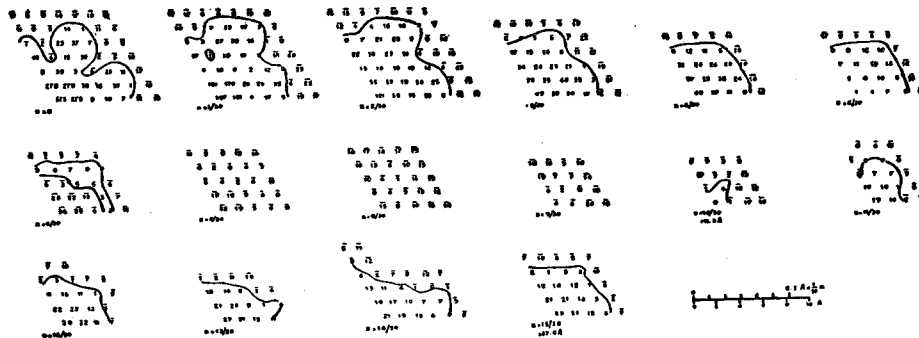


FIG. 1. Sections of the Patterson-Harker map of the "wet" insulin crystal in the neighborhood of the trigonal axis, parallel to the basal plane, calculated from Crowfoot's intensities.

pairs of  $C_1$  cages forming *intramolecular* parallel intergrowths on cube faces, rather than a single  $C_2$  cage.<sup>7</sup> Either of the first two suggestions places cyclic hexapeptides carrying closely packed *R*-substituents on antipodal faces normal to the trigonal axis, which interact in Patterson space to yield a local maximum at rather more than 12A from the origin which may be compared with the maximum in the region *C* which falls at  $z \sim \frac{2}{3}$ , i.e., at 13.6A from the origin.

\* This work is supported by the Office of Naval Research under Contract N8onr-579.

<sup>1</sup> Crowfoot and Riley, *Nature* **144**, 1011 (1939).

<sup>2</sup> Crowfoot, *Chem. J.* **G15**, 215 (1946).

<sup>3</sup> D. Wrinch, *Proc. Roy. Soc. London* **A161**, 505 (1937).

<sup>4</sup> D. Wrinch, *Science* **107**, 445 (1948).

<sup>5</sup> Oncley, *Science* **106**, 509 (1947).

<sup>6</sup> D. Wrinch, *Phil. Mag.* **26**, 325 (1938).

<sup>7</sup> D. Wrinch, *J. Am. Chem. Soc.* **60**, 2005 (1938).

## Vibrational Bands Measured with a Thallium Bromide-Iodide Prism

EARLE K. PLYLER

National Bureau of Standards, Washington, D. C.

August 11, 1948

IN recent papers<sup>1</sup> the writer has shown the method of calibration and use of the thallium bromide-iodide prisms for measurements to 40 microns. It was also found that polyethylene and polystyrene, in thin layers, are highly transparent in the 24- to 40-micron region and are well suited for window materials.

TABLE I. List of observed bands.

Substance	Wave-length ( $\mu$ )	Wave number ( $\text{cm}^{-1}$ )
Trichloroethylene	22.3	448
	25.9	386
	36.0	278
Tetrachloroethylene	23.4	427
	24.8	403
	28.8	347
	34.8	287
Benzene	24.8	403
Isobutylbenzene	22.5	444
	23.7	422
	24.9	402
	28.9	346
Methylene chloride	34.9	286
Carbon tetrachloride	30.5	328
	32.3	310
Bromoform	23.1	433
	25.8	388
	26.4	379
1,3,5-trimethylbenzene	30.0	333
	36.4	275
S-tetrabromoethane	22.4	446
	25.1	398
	35.5	282
Toluene	28.7	348
Chloroform	27.1	369
Carbon disulfide	25.2	397

A study has been made of the absorption spectra of about 30 substances in the long wave-length region, and bands have been found for molecules containing C=S, C-Cl, C-Br, and C-I and other atomic groups. In nearly all cases, cells of 0.4 mm or more in thickness are necessary for the observation of the bands. In Table I are given the wave-lengths and the frequencies of the observed bands for a selected group of substances.

Some of these frequencies have been predicted in studies of the molecular structure of these molecules.<sup>2</sup> In the gaseous state the bands are broad, and the regions of maximum absorption are not so clearly defined. The  $\text{CS}_2$  band, as measured in the vapor state at  $25.2\mu$ , is strong and is suitable for checking the calibration of the instrument. The absorption band of  $\text{CCl}_4$  at  $32.3\mu$  has been observed in the vapor. Propane has a band in the region of  $26\mu$  and some general absorption beyond  $30\mu$ . A detailed discussion of these absorption bands, as well as those of other substances comprising a total of thirty, will be given in a publication now in preparation.

<sup>1</sup> E. K. Plyler, *J. Chem. Phys.* **15**, 885 (1947), *J. Opt. Soc. Am.* **38**, 664 (1948).

<sup>2</sup> W. J. Taylor and R. S. Pitzer, *J. Research Nat. Bur. Stand.* **38**, 1 (1947); G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

## Mass Spectrometric and Infra-Red Study of Rates of Deuterium Exchange, Isomerization, and Hydrogenation of the *n*-Butenes

VERNON H. DIBELER\* AND T. IVAN TAYLOR

Department of Chemistry, Columbia University, New York, New York  
August 18, 1948

MUCH work has been reported on the nickel-catalyzed deuterium exchange, isomerization, and hydrogenation of the *n*-butenes. The use of mass spectrometric and infra-red analyses to determine the rate constants for the initial stages of these processes seemed to us to offer certain advantages over methods used in previous studies. In particular, mass spectral data should give information on the rates of exchange and addition as well as the position of the exchanged deuterium atom in the molecule. The "hydrogen-switch" mechanism recently proposed by Turkevich and Smith<sup>1</sup> for isomerization and tritium exchange is supported by our results. In certain respects we differ from the results of earlier studies by Twigg<sup>2</sup> and others.<sup>3</sup>

The reactions were carried out with equimolar quantities of hydrogen and olefin in a 400-cc Pyrex vessel containing an 80-cm length of 0.25-mm diameter nickel wire activated by heating alternately in oxygen and hydrogen. Rates of formation of deuterobutenes and of butane were observed by mass spectrometric analysis. Infra-red absorption at  $925 \text{ cm}^{-1}$  was used to follow the rate of isomerization of 1-butene to 2-butene.

During the initial stages of the reaction between deuterium and 1-butene, in the temperature range 93 to  $130^\circ\text{C}$ , the rate of isomerization was only slightly (1.0 to