added. To this mixture, with stirring, was added 120 g. of ethyl bromide, over a period of four hours. After standing two days, the excess sodamide was decomposed by the addition of 200 ml. of water. The mixture was extracted with ether, the ether solution dried, and the ether removed on a steam-bath. The residue was distilled, giving 8.0 g. (7% yield), b. p. 165–166° (755 mm.),[16] $n^{25}D$ 1.4897, d^{26}_4 0.9121.

The picrate was easily isolated as small yellow needles, m. p. 64°.[16]

Anal. Calcd. for $C_{14}H_{14}N_4O_7$: C, 48.00; H, 4.03; N, 16.0. Found: C, 47.89; H, 4.01; N, 15.8.

The chloroplatinate formed very quickly, and resulted in orange plates, m. p. 163–164°.[17]

Anal. Calcd. for $C_{16}H_{24}Cl_6N_2Pt$: Pt, 29.9. Found: Pt, 30.2.

The chloroaurate came down as a yellow powder, m. p. 77°.

Anal. Calcd. for $C_8H_{12}Cl_4NAu$: Au, 42.7. Found: Au, 42.5.

2-Vinylpyridine (X).—A sample from the Reilly Tar and Chemical Corporation was fractionated, and the constant boiling cut, b. p. 60° (17 mm.), used in this work,[18] $n^{31}D$ 1.5442, d^{31}_4 0.9661.

The picrate was isolated as a yellow powder, m. p. 152–154°.

Anal. Calcd. for $C_{13}H_{10}N_4O_7$: C, 46.71; H, 3.02. Found: C, 46.73; H, 3.01.

(16) Chichibain, ref. 12, reports a b. p. 173° and a m. p. 76° for the picrate.

(17) Ladenburg, *Ann.*, **247**, 21 (1888), reports a m. p. of 159–160°.

(18) Ladenburg, *Ber.*, **22**, 2585 (1889), reports a b. p. 79–82° (29 mm.).

The chloroplatinate melted at 174–175°, and the chloroaurate melted at 143°.[19]

Spectra.—The ultraviolet absorption spectra were obtained with a Beckmann quartz spectrophotometer. All physical constant measurements of the above alkyl pyridines were performed immediately after their isolation. Solutions of known concentrations were made by dissolving weighed quantities of compound in absolute alcohol in a volumetric flask. Dilutions were made volumetrically to give suitable density readings. The solutions were poured into one of two matched silica absorption cells and the second cell was filled with the solvent. Extinction coefficients were calculated from the equation

$$\epsilon = d/cl$$

where c is the concentration of the solute, in moles per liter, l is the thickness of the cell, in centimeters, and $d = \log_{10}(I_0/I)$. I_0 is the intensity of light passing through the solvent, and I is the intensity of light passing through the solution.

Summary

2-Cyclopropylpyridine was prepared and its ultraviolet absorption spectrum compared with those of 2-*n*-propylpyridine and 2-vinylpyridine. The maximum of 2-cyclopropylpyridine falls in a position between the two comparison compounds. This effect can be interpreted in terms of additional resonance due to hyperconjugation.

(19) Ladenburg, *ibid.*, reported the chloroplatinate m. p. 174°, and the chloroaurate, m. p. 144°.

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An Electron Diffraction Investigation of the Structure of Adamantane

BY WERNER NOWACKI AND KENNETH W. HEDBERG

The crystal structure of adamantane ($C_{10}H_{16}$, see Fig. 1) has been investigated by Nowacki,[1] who found a C–C bond distance of 1.54 ± 0.02 Å. on assumption of tetrahedral bond angles, and by Giacomello and Illuminati,[2] who obtained similar results by Fourier methods. A significant difference has been found between C–N distances in the crystal[3] and vapor[4] of hexamethylenetetramine, a molecule whose configuration is closely similar to that of adamantane, and although no such difference would be expected in adamantane, it seemed worth while to study it by electron diffraction in the vapor phase.

The photographs obtained show twelve maxima and shelves extending to q values of about 90 $(q = (40/\lambda)\sin \varphi/2 = (10/\pi)s)$.

Experimental

The sample of adamantane, which had been synthesized by Prelog and Seiwerth,[5] was vapor-

ized by use of a high temperature nozzle[6] in the apparatus described by Brockway.[7] The camera distance was about 11 cm. and the electron wave length[8] about 0.06 Å. Corrections were made for film expansion.

Radial Distribution Curve

The radial distribution curve (Fig. 2) was calculated from the equation[9,10] by use of punched

$$rD(r) = \sum_{q=1,2\ldots}^{q\,max} I(q) \exp(-aq^2) \sin\left(\frac{\pi}{10}\,q\,r\right)$$

cards[10,11]; the quantities $I(q)$ were taken from the visual curve (Fig. 2) drawn to represent the

(1) W. Nowacki, *Helv. Chim. Acta*, **28**, 1233 (1945).

(2) G. Giacomello and G. Illuminati, *Ricerca Sci.*, **15**, 559 (1945).

(3) P. A. Shaffer, Jr., THIS JOURNAL, **69**, 1557 (1947).

(4) V. Schomaker and P. A. Shaffer, Jr., *ibid.*, **69**, 1555 (1947).

(5) V. Prelog and R. Seiwerth, *Ber.*, **74**, 1644, 1769 (1941).

(6) L. O. Brockway and K. J. Palmer, THIS JOURNAL, **59**, 2181 (1937).

(7) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(8) For wave length calibration see C. S. Lu and E. W. Malmberg, *Rev. Sci. Instruments*, **14**, 271 (1943); the lattice constants of zinc oxide given by Lu and Malmberg in kx units were converted to Ångström units.

(9) R. Spurr and V. Schomaker, THIS JOURNAL, **64**, 2693 (1942).

(10) P. A. Shaffer, Jr., V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

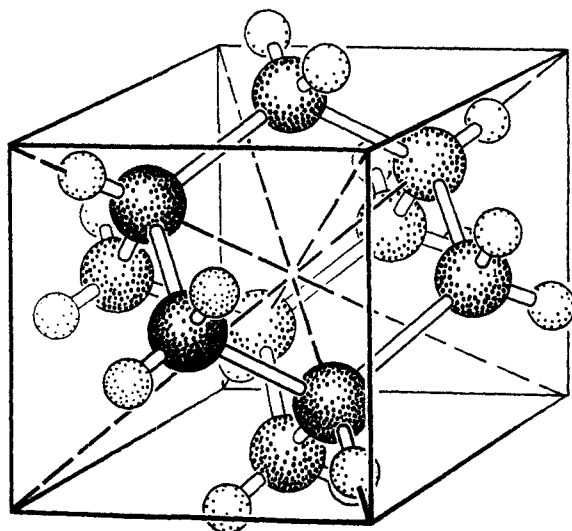(11) P. A. Shaffer, Jr., V. Schomaker and L. Pauling, *ibid.*, **14**, 648 (1946).

Fig. 1.—Adamantane.

appearance of the photographs, and the constant a was chosen to give exp $(-aq^2) = 1/10$ at $q = 90$. The resulting curve shows major peaks at 1.53 and 2.52 Å. which correspond to the bonded and to the shortest non-bonded $C \cdots C$ distances in a model such as C with tetrahedral bond angles; in model C these distances are 1.540 and 2.515 Å. There are additional peaks at 1.00, 2.92 and 3.46 Å., and a broad feature at 2.20 Å. With the exception of the first none of these is sufficiently well resolved for a determination of interatomic distances, though they agree well with our final model, as shown by the vertical lines. The heavy lines denote the $C \cdots C$ distances and the light, the $C \cdots H$; the lengths of the lines indicate the relative weights of the distances.

The deviation of the peak at 1.00 Å. from the value 1.09 Å. normally obtained from bonded $C \cdots H$ interactions closely parallels the result obtained by Schomaker and Shaffer[4] in their study of hexamethylenetetramine.[12]

Correlation of Visual and Intensity Curves

Intensity curves were calculated[10,11] from the

$$I(q) = \sum_{i,j}' \frac{Z_i Z_j}{r_{i,j}} \exp. \ (-a_{i,j}q^3) \sin \left(\frac{10}{\pi} \ qr \right)$$

equation[9] for a model of symmetry $T_d - \overline{4}3m$ assuming C–C = 1.54 Å. throughout, C–H = 1.09 Å. except for model G, and $\angle$HCH 109°28' except for model H. In models A to F the $C_2C_3C_2$

(12) The visual curve for adamantane was drawn without previous knowledge of the appearance of the hexamethylenetetramine photographs or of the corresponding intensity curves, although subsequently the photographs of the two substances were carefully compared and found to be closely similar. The errors in the two visual curves which correspond to the errors at 1.0 Å. in the two radial distribution functions are evidently nearly alike. Perhaps this is because they represent errors of interpretation which are in some way peculiar to the types of features shown by hexamethylenetetramine and adamantane.

bond angle is varied from 106°28' to 112°28'. Models G and H, which have tetrahedral C–C–C angles, are characterized by a shortened C–H distance (1.05 Å.) and an increased H–C–H angle (114°28'), respectively. Terms representing all bonded and non-bonded atomic interactions except H $\cdots$ H were included in the calculations. An effective value of $Z = 1.2$ was employed for hydrogen in order to approximate better its scattering power relative to carbon for small q. The coefficient $a_{i,j}$ was given the value 0.00016 for bonded C–H, 0.00030 for all non-bonded $C \cdots H$ interactions,[13] and zero otherwise.

TABLE I
ELECTRON DIFFRACTION DATA FOR ADAMANTANE

Max.	Min.	$q$obsd.	$q$calcd. (Model C)	$q$calcd./$q$obsd.[a]
	1	6.5	5.3	(0.815)
1		9.6	8.5	(0.885)
	2	13.3	12.6	(0.947)
2		17.8	17.8	1.000
	A	21.9	22.2	1.014
A		25.1	25.5	(1.016)
	3	27.8	27.2	(0.798)
3		30.3	29.3	(0.967)
	4	32.8	33.7	[1.027]
4		35.7	35.3	[0.989]
	5	38.7	38.1	0.984
5		42.2	42.0	0.995
	6	45.8	46.2	1.009
6		49.3	49.8	1.010
	7	53.3	53.2	0.998
7		57.4	57.0	0.993
	8	61.4	61.2	0.997
8		66.0	67.3	(1.020)
	9	70.6	72.3	[1.024]
9		74.2	75.2	[1.013]
	10	77.7	78.1	1.005
10		81.7	82.2	1.006
	11	85.5	86.7	1.014
11		90.1	90.5	1.004

Average   1.004

Average deviation   0.008

[a] Parenthesized values were omitted in evaluation of averages, bracketted values were given half weight.

Comparison of the calculated curves with the visual curve shows model A to be unacceptable; minimum 8 appears in the calculated curve as far too broad and the relative depths of minima 9 and 10 are inverted. Curve B is somewhat better than A but the disagreement in the relative depths of minima 9 and 10 is still present. Curve C is generally satisfactory.[14] Curve D is acceptable

(13) Because of the relative rigidity of the carbon skeleton of adamantane we believe the value 0.00030 for $a_{i,j}$ to be a reasonable one for all the non-bonded $C \cdots H$ interactions.

(14) The main points of disagreement in the correlation of model C with the observed intensity distribution are seen to involve (1) the relative depths of minima 1 and 2, (2) the strength of shelf A, (3) the shape of maximum 8, and (4) the relative depths of minima 5 and 6. The first two items do not appear to be serious; estimates of the depth of the first minimum are subject to considerable error, and a
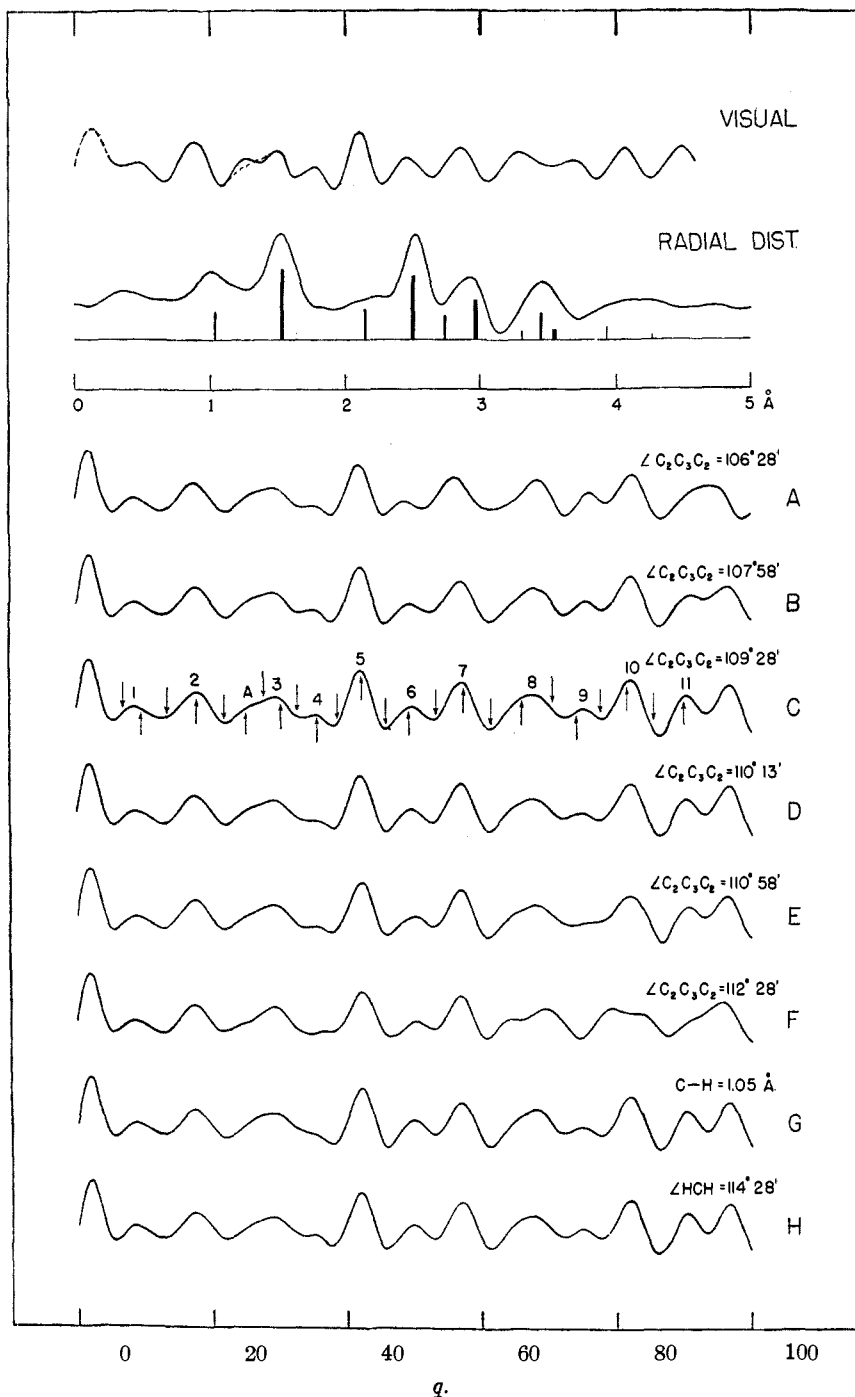
Fig. 2.—Electron diffraction curves for adamantane.

reexamination of the photographs indicates the exaggeration of shelf A to be a simple misinterpretation (the dotted line is felt to be a more accurate representation of this feature). Item (3) also arises from errors of interpretation, as shown by comparing photographs of adamantane and hexamethylenetetramine; the appearance of maximum 8 is closely similar and was satisfactorily represented by Schomaker and Shaffer[4] in their visual intensity curve for hexamethylenetetramine. It is difficult to explain the reversal of minima 5 and 6 (item (4)). Perhaps the trouble is due to a tendency to compensate incorrectly for the background intensity, which is difficult to estimate in patterns as complicated as that of adamantane.

although maximum 4 is a poorer representation of the appearance of the photographs than the same maximum in C. Curves E and F are unsatisfactory. Curves G and H are both acceptable although G is not as satisfactory as C in the region of maximum 4. We conclude that in the adamantane molecule in the gas phase $\angle C_2C_3C_2 = 109.5 \pm 1.5°$, the upper limit of this determination being especially conservative. The $\angle HCH$ and C–H/

C–C determinations cannot be made to within sizable limits of error.

A comparison (Table I) of the observed q values with those calculated for model C (all bond angles tetrahedral, C–C = 1.54 Å., C–H = 1.09 Å.), a consideration of the radial distribution function, and comparisons of visual and calculated intensity curves lead to the following structural parameters and probable limits of error: symmetry $T_d - \bar{4}3m$ (assumed), ∠HCH = 109°28' (assumed), C–H = 1.09 Å. (assumed), C–C = 1.54 ± 0.01 Å., ∠C₂C₃C₂ = 109.5 ± 1.5°.

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Summary

An electron diffraction investigation of the structure of the adamantane molecule in the gas phase has led to values for the structural parameters in agreement with those found in the crystal. On the assumption of symmetry $T_d - \bar{4}3m$, of C–H = 1.09 Å., and of ∠HCH = 109.5°, the results are C–C = 1.54 ± 0.01 Å., and ∠C₂C₃C₂ = 109.5 ± 1.5°.

The System Cesium Fluoride–Hydrogen Fluoride

By R. Virginia Winsor and George H. Cady

Mathers and Stroup[1] have shown that solutions made by melting acid fluorides of cesium may be used at approximately room temperature as electrolytes for the preparation of fluorine. They found that the acid fluorides of cesium have lower melting points than the corresponding salts of potassium, but in their work identified only the previously known compound, CsF·HF. A more thorough study of the system comprises the subject matter of the present article.

Experimental

A 36.0-g. sample of cesium fluoride was prepared from pulverized pollucite following a procedure based upon work of Wells[2] and recommended by Geo. McPhail Smith. The mineral was digested with an equal weight of 6 N hydrochloric acid at about 95° for approximately three days. Solid remaining undissolved was separated by filtration and the filtrate was evaporated to dryness. The product was then dissolved in four times its weight of 4 N hydrochloric acid and, after filtering, one gram atom of iodine was added for each mole of cesium chloride present. The liquid was then heated while an excess of chlorine was passed. As the resulting solution was allowed to cool, the compound CsICl₂ crystallized. This salt was purified by three recrystallizations in the presence of a little ICl in solution. Cesium chloride was produced by the thermal decomposition of CsICl₂. The chloride was converted to the nitrate which

(1) F. C. Mathers and P. T. Stroup, *Trans. Am. Electrochem. Soc.*, **66**, 245 (1934).

(2) H. L. Wells, *Am. Chem. J.*, **26**, 265 (1901).

was fused with oxalic acid to form the carbonate. Aqueous hydrofluoric acid was allowed to react with the carbonate and the resulting solution was poured into the silver vessel shown in Fig. 1. Evaporation of the solution left the fluoride. Hydrogen fluoride was then added. The vessel was heated and hydrogen fluoride was removed by vacuum distillation. This process of adding and then removing hydrogen fluoride was repeated a few times with the result that the vessel plus the cesium fluoride came to constant weight.

Hydrogen fluoride was obtained as the vapor by distillation from a cylinder of the commercial anhydrous acid. About half of the material originally present in the cylinder had been removed by evaporation before starting the work on the system.

Cooling or warming curves were determined using the apparatus shown in Fig. 1. This comprised a silver cylinder, A, of 105 ml. capacity equipped with a thermocouple well, B, and a monel metal tube, C, through which materials were added or removed. The composition of the charge was determined by weighing the vessel and its contents. Temperatures were measured with a calibrated copper–constantan thermocouple connected to a potentiometer. Each cooling curve was established by first heating the vessel and then allowing it to cool slowly while being held firmly in a Dewar flask or other well-insulated vessel which was moved rapidly back and forth in a mechanical shaker. Temperatures below that of the room were reached by placing solid carbon dioxide in the Dewar vessel in such a location that the