be less stable than I. These assumptions are consistent with the relative yields and stabilities observed for the two compounds.

The structure proposed for $(CH_3N)_3S_5$ (I) is somewhat similar to B which Levi[5] and Becke-Goehring and Jenne[6] obtained from S_2Cl_2 and $C_2H_5NH_2$. The $-SSSN-$ grouping in the structure proposed for $(CH_3N)_3S_5$ (II) has been suggested as a possible form of the $-S_3N-$ ligand in $Ni(S_3N)_2$. Piper[24] isolated this latter compound from the reaction of S_4N_4 with $NiCl_2$.

Although we have not examined the analogous reaction of SCl_2 with $C_2H_5NH_2$, our results raise some doubt that the unstable oil obtained by Lengfeld and Stieglitz was a single molecular species.

(24) T. S. Piper, THIS JOURNAL, **80**, 30 (1958).

DAYTON, OHIO

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

The Molecular Structure of Pivalonitrile by Electron Diffraction[1]

BY R. L. LIVINGSTON AND C. N. RAMACHANDRA RAO[2]

RECEIVED OCTOBER 8, 1958

The molecular structure of pivalonitrile has been studied by the sector-microphotometer method of electron diffraction. The central C–C distance has been found to be 1.46 ± 0.020 Å. The other parameters are: C–C = 1.540 ± 0.010 Å., C–N = 1.160 ± 0.007 Å. and ∠C–C–CN = 109.5 ± 1.5°.

Electron diffraction and microwave investigations of CH_3CN,[3,4] CF_3CN[3,5] and CH_3CH_2CN[6] have shown that there is a considerable contraction in the central C–C distances in these molecules; such contractions have been regarded as evidence for hyperconjugation. It seemed worth while to investigate the molecular structure of pivalonitrile (α,α-dimethylpropanenitrile) in order to determine whether there is similar contraction of the C–C in this compound.

Experimental

The sample of pivalonitrile was obtained from the du Pont Company. After a few vacuum distillations, the sample was found to be at least 99% pure by a cooling curve analysis.

Several electron diffraction patterns were taken with an r^3-sector at two camera distances, employing electrons of wave length 0.05452 Å. Kodak Lantern Slide Contrast Plates were used with camera distances of 10.19 and 25.10 cm. Microphotometer traces of four of the best plates were taken using a Leeds and Northrup microphotometer. The transmittancies were converted to arbitrary intensity units[7] and the results at each camera distance were averaged. The total range of data extended from $q = 16$ to $q = 112$.

The radial distribution procedure was employed by calculation of curves by the equation[8]

$$rD(r) = \sum_{q=1,2,\ldots}^{q_{\max}} I_m(q) \exp(-bq^2) \sin \frac{\pi q r}{10} \qquad (1)$$

where $rD(r)$ is the radial distribution function, r is the internuclear separation and $\exp(-bq^2) = 0.10$ at $q = q_{\max}$.

For the radial distribution calculations, the intensity data between $q = 0$ and $q = 15$ were taken from a theoretical scattering curve calculated by[8]

$$I_m(q) = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} \exp(-b_{ij} q^2) \sin \frac{\pi q r_{ij}}{10} \qquad (2)$$

The initial radial distribution curve showed some extraneous features. By treating these extraneous features as intensity data by means of equation 1, an estimate was obtained of the changes to be made in the background line. The second and final radial distribution curve is shown in Fig. 1 and the final experimental intensity curve is shown in Fig. 2.

Results and Discussion

The radial distribution curve did not give directly any of the parameters of pivalonitrile. It showed five peaks and two were resolved by the procedures of Karle and Karle.[9] The first peak was decomposed to give the C–H and the C–N distances. The second peak at 1.52_3 Å. was decomposed to give two types of C–C distances. The areas of these decomposed peaks are in good agreement with the calculated nZ_iZ_j/r_{ij} values (Table I). The third and fourth peaks are each due to the contributions from a number of distances and no attempt was made to decompose them. The fifth peak is rather small and represents a non-bonded N–H distance. The position of this peak is not reliable since small oscillations in the zero line of the radial distribution curve can change the shape of such a peak considerably. The radial distribution curve gives the C–C and the central C–C bonds as 1.54 and 1.46 Å., respectively. The C–H and the C–N distances are found to be 1.09 and 1.16 Å. The radial distribution curve does not, however, provide any information about the C–C–CN angle (α). The relevant results from the radial distribution curve are summarized in Table I. The table also lists the root mean square amplitudes of vibration, Δr_{ij}, obtained by the Karle's method.[7,10]

TABLE 1

RESULTS OF THE RADIAL DISTRIBUTION CURVE FOR PIVALONITRILE

Distance	r_{ij}	Δr_{ij}	Area	nZ_iZ_j/r_{ij}
C–H	1.09	0.075	88.4	88.6
C–N	1.16	.00	49.8	51.4
C–C(central)	1.46	.05	34.4	35.7
C–C	1.54	.05	100	100

---

(1) Contains material from the doctoral dissertation of C. N. R. Rao. Presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

(2) Purdue Research Foundation Fellow in Chemistry, 1956–1957; Standard Oil Foundation Fellow in Chemistry, 1957–1958.

(3) M. D. Danford and R. L. Livingston, THIS JOURNAL, **77**, 2944 (1955).

(4) M. Kessler, H. Ring, R. Trambarulo and W. Gordy, *Phys. Rev.*, **79**, 54 (1950).

(5) J. Sheridan and W. Gordy, *J. Chem. Phys.*, **20**, 591 (1952).

(6) R. G. Lerner and B. P. Dailey, *ibid.*, **26**, 678 (1957).

(7) J. Karle and I. L. Karle, *ibid.*, **17**, 1052 (1949).

(8) P. A. Shaffer, Jr., V. Schomaker and L. Pauling, *ibid.*, **14**, 659 (1946).

(9) I. L. Karle and J. Karle, *ibid.*, **18**, 963 (1950).

(10) J. Karle and I. L. Karle, *ibid.*, **18**, 957 (1950).

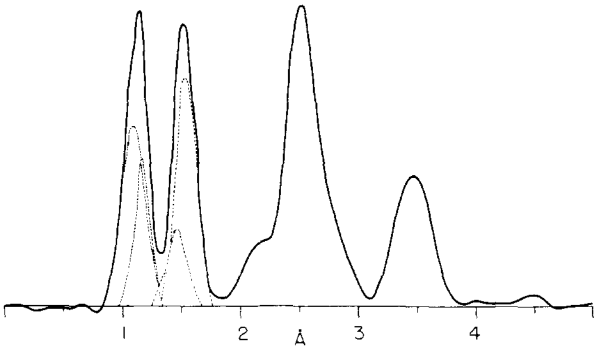

Fig. 1.—Radial distribution curve for pivalonitrile.

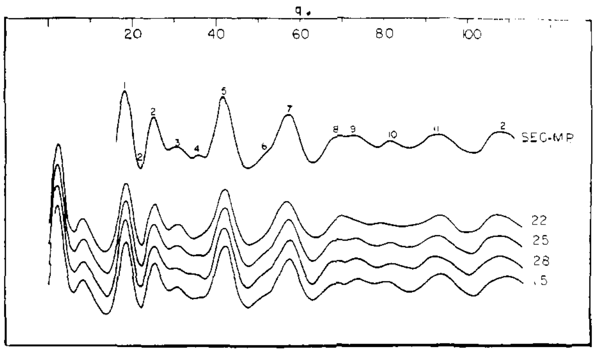

Fig. 2.—Observed and calculated intensity curves for pivalonitrile.

In order to determine the range of uncertainties on the parameters obtained by the radial distribution method and also to determine the angle α, the correlation procedure was employed. The normal C–C distance was kept constant at 1.54 Å. for all the models. The molecule was assumed to have the symmetry of the C_{3v} point group. Several theoretical scattering curves were calculated using equation 2, assuming a C–N distance of 1.16 Å. Relevant vibration factors based on the radial distribution results were used for the different atom pairs. The parameter field chosen in the plane with C–N = 1.16 Å. (2X plane) is shown in Fig. 3.

In order to determine the uncertainty in the C–N distance, a few models were calculated in two additional planes, one 0.02 Å. below (1X plane) and the other 0.02 Å. above (3X plane) the C–N = 1.16 Å. plane. The calculated intensity curves for a few experimental models are shown with the experimental curve in Fig. 2.

The qualitatively acceptable models in the 2X plane are within the region of the dotted line in Fig. 3. Comparison of the scattering curve for model 25 with the experimental curve shows their extraordinary similarity (Figure 2). Model 25 also exactly corresponds to the results of the radial distribution curve with regard to the C–H, central C–C, C–C and C–N distances and shows an average deviation of about 0.003 from the mean $q_{\text{calcd}}/q_{\text{obsd}}$.

In curves 27, 28 and 29, maxima 3 and 4 are not well defined and minima 5 and 9 are too prominent; in addition the shape of maximum 12 is not acceptable. In curves 21, 22 and 23, maxima 4 and 9 and minimum 5 are not present and minimum 10 and maximum 10 are not well defined; further, a shoulder appears on maximum 11. Curves 24 and 26 show slight disagreement with the experimental curve in maxima 4, 10 and 12 and minima 5 and 9. These deviations are much smaller than in the other curves discussed above and models 24 and 26 are therefore considered as extreme borderline cases.

In the plane with C–N = 1.14 Å. (1X plane) and in the plane with C–N = 1.18 Å. (3X plane), the variations in the calculated intensity curves with parameters are similar to those found in the 2X plane. No models in these planes, including models 15 and 35, were acceptable.

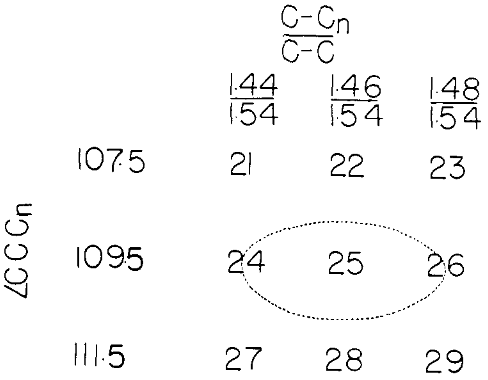

Fig. 3.—Parameter charts for pivalonitrile: C_n refers to the carbon atom which is attached to the nitrogen atom. In the principal parameter plane investigated, C–N = 1.16 Å.; a few additional models were calculated in the planes with C–N = 1.14 Å. and with C–N = 1.18 Å.

In Table II the experimentally determined q values are listed along with the q_c/q_0 ratios for the acceptable models. The parameters calculated from these models are given in Table III. These values were used to estimate the relative uncertainties associated with the parameters obtained by the radial distribution method and also to determine the angle α. The final parameters of pivalonitrile based on the radial distribution method and the correlation procedure are

C–N = 1.160 ± 0.007 Å.
Central C–C = 1.460 ± 0.020 Å.
C–C = 1.540 ± 0.010 Å.
$\angle\alpha = 109.5 \pm 1.5^\circ$

TABLE II

QUANTITATIVE ELECTRON DIFFRACTION DATA FOR PIVALONITRILE

Max.	Min.	q_0	q_c/q_0 24	25	26
1		18.3	1.006	1.002	0.997
	2	21.9	0.998	0.998	.987
2		25.1	1.001	1.001	.993
	3	28.4	1.011	1.005	1.000
3		30.6	1.005	0.997	0.994
5		41.6	1.007	1.003	1.000
7		57.3	1.000	0.997	0.997
	8	62.8	1.007	1.003	.999
	10	78.2	...	0.998	.990
10		81.1	...	1.005	1.004
	11	85.6	0.990	0.998	1.014
11		92.8	.997	.997	0.997
	12	101.2	.995	.997	0.994
		Mean	1.002	1.000	0.997
Av. dev. from the mean			0.005	0.003	0.005

TABLE III

PARAMETERS FROM THE ACCEPTABLE MODELS FOR PIVALONITRILE

Parameter	Model 24	25	26
∠C–C–CN, degrees	109.5	109.5	109.5
C–N, Å.	1.162	1.160	1.157
C–N(central), Å.	1.443	1.460	1.476
C–C, Å.	1.543	1.540	1.535
C---CN, Å.	2.435	2.450	2.463

The microwave data[11,12] on pivalonitrile are not sufficient to determine its structure, but the results of the present investigation are in agreement with the one moment of inertia obtained from the microwave spectra.

The C–N distance of 1.16 Å. in pivalonitrile is the same as in other nitriles.[3–6] It is also interesting to note that all the derivatives of methylacetylene and acetonitrile whose structures have been studied[12,13] show a C–C bond distance of about 1.46 Å. for the bond adjacent to the triple bond. From the valence-bond point of view, one would expect the C–C bond distances to vary somewhat with electronegativity if all of the shortening were due to hyperconjugation. Coulson[14] has suggested that part of the contractions may be due to hybridization, while Dewar and Schmeising[15] have proposed that the contractions may be due entirely to hybridization which results in a change in the covalent radius of the carbon atom.

The authors' thanks are due to the du Pont de Nemours Company, Inc., Electrochemical Division, Wilmington, Delaware, for kindly supplying the sample of pivalonitrile.

LAFAYETTE, INDIANA

---

[11] T. Sparstad and E. Amble, *J. Chem. Phys.*, **27**, 317 (1957).

[12] W. Zeil and Pfrommer, *Z. Elektrochem.*, **61**, 938 (1957).

[13] Recent electron diffraction work in this Laboratory yielded a C–C distance of 1.46₅ Å. in CCl_3CN and a recent microwave investigation of $CH_2(CN)_2$ (N. Muller and D. E. Pritchard, THIS JOURNAL, **80**, 3483 (1958)) gave a C–C distance of 1.46 Å. Results on other derivatives of methylacetylene and acetonitrile are summarized in reference 12.

[14] C. A. Coulson, "Valence," Clarendon Press, Oxford, 1952.

[15] M. J. S. Dewar and A. N. Schmeising, Conference on Hyperconjugation, Indiana University, June, 1958.