The same order is likewise observed for variation of C with a given A and B.[11] It seems reasonable that the order for variation of B can be deduced from a comparison of the velocity of oxidation of iodide ion by chloric, bromic and iodic acids since it is probable that the important step in these reactions is substitution of iodine for hydroxyl on the central halogen atom.[13] The order observed for the velocities of these reactions is the one given above. Hence the lower limit which has been established for the specific velocity of formation of trichloride ion is apparently also a valid lower limit for the specific velocities of formation of tribromide and triiodide ions. It should be pointed out, however, that this order does not necessarily prevail for the specific velocities of decomposition of the several trihalide ions.

An alternative explanation for the results of Long and Olson could be based on interchange between chloride ion and chloroacetanilide subsequent to chlorination. This mechanism is eliminated from further consideration in view of the fact that the reaction of bromide ion with chloroacetanilide occurs very slowly.

Summary

1. The chlorine–chloride ion interchange occurs through the mechanism of formation and decomposition of the trihalide ion. This is probably also the mechanism for bromine–bromide ion and iodine–iodide ion interchanges.

2. Lower limits have been established for the velocity constants of the two reactions: (a) formation of trichloride ion: $k > 4 \times 10^5$ liters mole^{-1} min.$^{-1}$ and (b) decomposition of trichloride ion: $k > 4 \times 10^7$ min.$^{-1}$ at 17°.

3. The lower limit given above probably holds also for the velocities of formation of tribromide and triiodide ions.

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[13] This opinion is also held by Professor W. C. Bray who has drawn this conclusion from the results of his own unpublished investigations.

[CONTRIBUTION FROM THE LABORATORIES OF CHEMISTRY AND PHYSICS OF THE UNIVERSITY OF MICHIGAN]

The Molecular Structures of Methyl Isocyanate and Cyanic Acid by the Electron Diffraction Method. The Structural Chemistry of Cyanic Acid and its Derivatives

BY EUGENE H. EYSTER,[1] R. H. GILLETTE AND L. O. BROCKWAY

The theoretical picture of molecules whose ground states are achieved by resonance among several valence bond structures is now so well developed that it is not only possible to predict with confidence the qualitative aspects of the structures of cyanic acid and its derivatives, but also to anticipate many quantitative details of these structures. Indeed, it has been pointed out[1a] that the covalent cyanate group should be expected to have a linear configuration of over-all length 2.36 Å., with the carbon atom located approximately at the center. While this prediction is entirely compatible with the rather indirect evidence furnished by the vibration spectrum of the methyl ester of cyanic acid,[1a] it can hardly be reconciled with the assertion, by Herzberg and Verleger,[2] that cyanic acid itself is an extremely asymmetric molecule in the dynamic sense, a statement which has as its basis the unusually complex rotational structure of the third N–H harmonic band of cyanic acid. This structure seems, at least on superficial examination, to bear little resemblance to that of the corresponding band of hydrazoic acid, though the structural theory predicts very similar configurations for these two compounds. Since the cyanic acid bands have not been actually analyzed, and since there have been, indeed, no direct physical determinations of the structure of the covalent cyanate group,[3] it has appeared desirable to study the structures of the free acid and its methyl ester by the electron diffraction method. The investigations described in the following pages provide a complete confirmation of both the qualitative and quantitative aspects of the structural theory as applied to the covalent cyanate group, and we have also taken this opportunity to discuss its further applications to the structural

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[1a] Eyster and Gillette, *J. Chem. Phys.*, **8**, 369 (1940).

[2] Herzberg and Verleger, *Physik. Z.*, **3** , 444 (1937).

[3] The structure of the ionic cyanate group in potassium cyanate has indeed been studied by X-ray methods by Hendricks and Pauling, THIS JOURNAL, **47**, 2904 (1925), but their distance determinations in the cyanate group are not of sufficient precision to lead to significant conclusions concerning the relative contributions of various resonating structures to the ground state of the ion.

chemistry of certain interesting derivatives of cyanic acid. In our opinion, the appearance of the Herzberg–Verleger band can constitute no real refutation of these results, for so complex a structure might also occur in the bands of a dynamically symmetric molecule.[4]

Experimental

Methyl isocyanate was prepared by the method of Slotta and Lorenz.[5] The crude product was dried over calcium chloride and purified by fractional distillation. Since this compound, like all the alkyl isocyanates, gradually polymerizes to an ester of isocyanuric acid, the sample was distilled into the final receiver immediately before the electron diffraction photographs were taken.

Cyanic acid was generated by the depolymerization of anhydrous cyanuric acid, prepared from urea by the method of Walther.[6] The cyanuric acid was heated strongly in a slow stream of carbon dioxide, and the cyanic acid was condensed from the resulting gas mixture at −80°. The dissolved carbon dioxide was pumped off at −20°, and the crude product was freed from suspended cyanuric acid and cyamelide by vacuum distillation from the trap at −20° to the final receiver at liquid air temperatures. The product was used at once, and its further polymerization was avoided by maintaining the sample at or below −19° while the photographs were being taken. To test for possible falsification of the photographs by residual carbon dioxide, a second preparation was made using helium as a carrier gas; the two samples gave indistinguishable results.

The photographs were obtained in a new electron diffraction apparatus which follows the Pasadena design[7] with some modifications. A new voltage regulator was used which held the d. c. high potential constant within 0.01% for periods up to thirty minutes; this accelerating potential is read on a Leeds and Northrup type K potentiometer with the aid of a voltage divider. The a. c. ripple, which was measured with a cathode ray oscillograph connected in series with a 50 kv. blocking condenser across the high potential output, was observed to be ±0.01% at 40 kv. The absolute value of the d. c. high potential was measured in terms of a laboratory standard cell (checked against six saturated cells calibrated by the Bureau of Standards) and of the resistance ratio in the voltage divider as determined on a Nalder precision bridge. The over-all uncertainty in the absolute value of the d. c. accelerating potential was less than 0.05%, and in the electron wave length the uncertainty was half that value. The effect of this very steady wave length was tested in photographs of gold foil, in which the first eighteen diffraction maxima were distinctly resolved (with the exception of 444 which was too faint), whereas the early Pasadena photographs[7] showed four unresolved doublets in the same range. The maximum deviation from the mean of the wave length values calculated from the observed rings was 0.25%. The uncertainty in interatomic distances obtained from photographs of gases is now almost entirely due to the uncertainty in measuring the negatives and in their correlation with theoretical intensity curves.

Other modifications in the apparatus include the use of a magnetic lens for focusing the electron beam on the photographic plate and a new style of gas nozzle which has no connection between the vapor tube and the camera except for two small openings through which the electrons pass in and out of the gas stream. The magnetic lens affords a more effective use of the electrons passing through the anode than does a simple collimating tube, and the number of electrons reaching the plate away from the central spot is much less for the same current in the main beam. The new gas nozzle also affords cleaner photographs with less general background because it is directly connected to a diffusion pump and allows less vapor to escape into the camera.

In the present investigation the electron tube was operated with a space current of from ten to twenty microamperes and an accelerating potential just above forty kilovolts corresponding to a wave length of 0.05924 Å. The camera distance was 10.19 cm. From thirty to forty measurements were made on each maximum and minimum appearing on the plates for both compounds.

Methyl Isocyanate.—The photographs of methyl isocyanate extend out to $s = 27$ and show seven distinct maxima and four minima which are suitable for measurement. Table I gives the measured values of s (equal to 4π $(\sin \Theta/2)/\lambda$) and the visually estimated intensities I_k. The qualitative features of the photographs are well represented by curve H of Fig. 2, in which, however, the deep first minimum is not shown. The strong first maximum followed by a long, rather formless shoulder leading into a clearly defined minimum, and the weaker maxima 3 and 5 poorly separated from their stronger neighbors 2 and 4 constitute the distinctive features of these photographs.

The radial distribution function for methyl isocyanate (Fig. 1) was calculated by the modified method of Schomaker,[8] in which corrected intensities, $C_k = s^2e^{-as^2} I_k$, replace the usual visual intensities I_k. The exponential damping factor a is chosen so that for the largest ring $e^{-as^2} = 0.1$. This radial distribution function shows strong,

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(4) Though our model for cyanic acid is very nearly symmetric, in the sense that its two larger moments of inertia are very nearly equal, it is by no means electrically symmetric, and the Herzberg–Verleger band is undoubtedly a parallel–perpendicular hybrid. The simplicity of the analogous hydrazoic acid band (see Eyster, *J. Chem. Phys.*, **8**, 135 (1940)) is due to the small relative intensity of the perpendicular component; if it were but slightly more intense than the parallel component, the whole band might well be reduced to a state of hopeless confusion. The dependence of these parallel–perpendicular intensity ratios for overtone bands upon molecular structure is at present most obscure, and that they should be similar in cyanic and hydrazoic acids need not be true.

(5) Slotta and Lorenz, *Ber.*, **58**, 1320 (1925).

(6) Walther, *J. prakt. Chem.*, [2] **79**, 128 (1909).

(7) Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

(8) Schomaker, American Chemical Society Meeting, Baltimore, April, 1939. The advantages of another method due to Walter and Beach, *J. Chem. Phys.*, **8**, 601 (1940), seem incommensurate with the additional complexities which it entails.

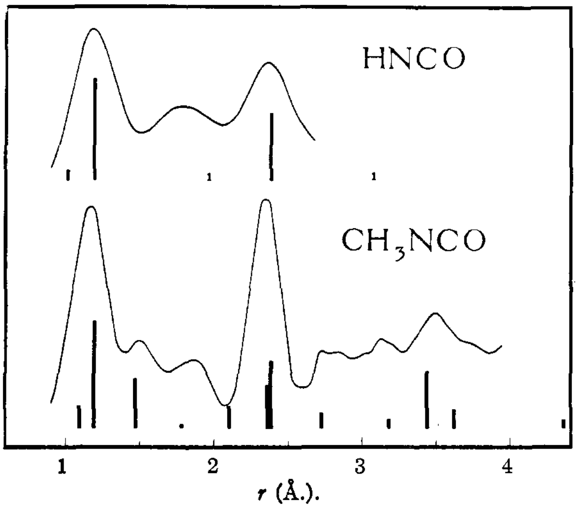

Fig. 1.—Radial distribution functions for methyl isocyanate and cyanic acid. The heavy lines correspond to the distances in the final models, and their heights are proportional to the appropriate products Z_iZ_j.

sharp maxima at 1.17 and 2.35 Å., and weaker ones at 1.49 and 3.49 Å.; the other peaks are probably spurious. By analogy with methyl azide[9] these peaks may be given a reasonable interpretation at once. The peak at 1.17 Å. is an unresolved blend of the C–O, C–N, and C′–H[10] distances, that at 2.35 Å. is a blend of the N–O and C′–C distances and that at 3.49 Å. is the C′–O distance, possibly blended with two O–H distances. The 1.49 Å. peak, though a bit weak, is probably a real C′–N peak. We shall require that our final structure be in reasonable agreement with these values.

With the methyl group assumed to be tetrahedral with C′–H distances equal to 1.09 Å., the C′–N distance equal to 1.47 Å., and the cyanate group linear, there remain three parameters to be evaluated from the photographs. For the present it is convenient to choose these as *r*, the N–O distance, *k*, the ratio N–C/C–O, and *α*, the angle between the cyanate group and the N–C′ bond. As a preliminary step, a base model with parameters $r = 2.37$ Å., $k = 1.025$, and $\alpha = 120°$ was chosen, and each parameter was then separately varied. Curve B of Fig. 2 shows the intensity distribution calculated for this base model, omitting at this stage all the hydrogen interactions except those due to C′–H and N–H (an omission which was found to have but small effect on the curves except in the vicinity of the long shoulder just beyond the first maximum). Curves A and C are similarly calculated functions for *α* equal to 130 and 110°, respectively. A comparison of the qualitative and quantitative features of these curves with those of the photographs indicates that a model about halfway between A and B would be an improvement on the base model. Curves D and E are similar intensity functions for models in which the parameter *r* has been varied to 2.30 and 2.44 Å., respectively. The qualitative features of the base curve have not been strikingly modified by these changes, but the quantitative agreement is obviously much worse for both the varied models. In curves F and G the parameter *K* has been varied to 1.115 and 0.943, respectively. In curve F the maxima 3 and 5 have become too strong relative to maxima 2 and 4, but curve G is very similar to the base curve B. This fact is not hard to understand, since the model of G differs from the base model only in a lengthening of the C′–C distance, and merely interchanges the C–O and C–N distances, whose coefficients on the intensity formula are not very

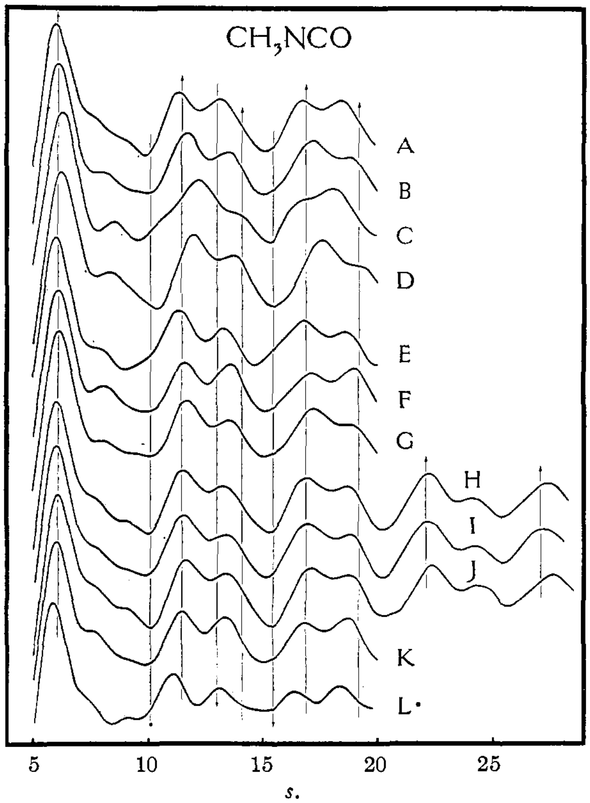

Fig. 2.—Theoretical intensity functions for models of methyl isocyanate; for description of the models see text. The arrows indicate measured maxima and minima.

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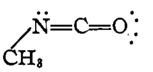
[9] Pauling and Brockway, This Journal, 59, 13 (1937).

[10] For brevity we shall distinguish the carbon atom of the methyl group with a prime.

different. As may well be foreseen, this experimental method will not differentiate structures related in this way. A completely linear model was also calculated, but was hopelessly wrong.

From these preliminary investigations it becomes quite clear that either model B or G with an increase of about 5° in α will be in essential agreement with the observed photographs, except for the fact that the weaker maxima 3 and 5 seem always to be closer to their stronger neighbors 2 and 4 than the measurements of the plates indicate, nor will any parameter variation within reason even begin to remedy this defect. We feel that this is an inherent error of visual measurement, associated with the St. John effect, and accordingly demand quantitative agreement for the strong maxima and only the correct relative intensities for the weaker maxima 3 and 5; correspondingly we shall omit the measurements of the weaker maxima in making the final scale adjustments.

Now the dimensions of the cyanate group in the base model B were not chosen at random, but were calculated by the Pauling method[11] on the assumption of equal resonance among the following three structures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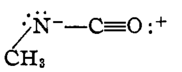
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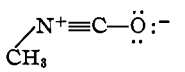
III

Since this method gives a structure for the cyanate group which is in essential agreement with the photographs, it now seems advantageous to replace our distance parameters r and k by the theoretically more significant coefficients x_{I}, x_{II}, and x_{III}, which specify the relative contributions of the above structures to the ground state of the cyanate group. These parameters are, to be sure, equivalent to r and k through relations of the Pauling type,[11] but since $0 \leqslant x_i \leqslant 1$ and $\sum_i x_i = 1$ the range of the parameters has been restricted; our preliminary studies show, however, that the true structure lies even within this restricted range.

The final parameter adjustments have been made with the aid of curves H through L of Fig. 2, which now contain all the hydrogen interactions for a fixed configuration and which, unless obviously wrong, have been calculated out to $s = 28$. The angle α has in all cases been chosen as 125° for reasons already mentioned, and also to give better agreement with the radial distribution function. Curve H, calculated for $^1/_3$, $^1/_3$, $^1/_3$ resonance, agrees very well with the observed photographs, as does curve I, for $^2/_5$, $^1/_5$, $^2/_5$ resonance. Curve J, for $^1/_5$, $^2/_5$, $^2/_5$ resonance, is also qualitatively correct, but when its scale is altered to give the best average quantitative agreement, it is found that the resulting model is almost identical with the scale adjusted model of curve H, except for a small expansion of the methyl group and the C′–N bond. Curves K and L, for $^1/_2$, 0, $^1/_2$ and $^2/_5$, $^2/_5$, $^1/_5$ resonance, respectively, are clearly unsatisfactory. Hence we are left with but two satisfactory models, H, with N–C and C–O distances of 1.20 and 1.17 Å., respectively, and I, with the distances 1.18 and 1.20 Å. Between these two models we feel incapable of making a clean-cut choice, so Table I contains the ratios s(calcd.)/s_0 for both models, and the resulting scale-adjusted internuclear distances. It should be noted that the inability to distinguish between curves H and I is reflected in an uncertainty in the position of the central carbon atom, the over-all length of the group being very nearly the same for both models. Hence we choose as our final values the averages of the distances for the two corrected models: N–C = 1.19 ± .03 Å., C–O = 1.18 ± .03 Å., and N–O = 2.37 ± .03 Å. The scale adjusting factors are so nearly unity that it would seem that our assumed C′–N distances were essentially correct at 1.47 Å. These interatomic distances are indicated for comparison with the

TABLE I

METHYL ISOCYANATE

Max.	Min.	s_0	I_k	C_k	s_{H}/s_0	s_{I}/s_0
	1	4.54	−15	−29	(...)	(...)
1		6.07	20	66	0.997	0.997
	2	10.10	−10	−74	0.990	0.980
2		11.46	10	86	1.003	1.009
	3	12.99	− 3	−30	(0.971)	(0.974)
3		14.08	5	54	(0.942)	(0.958)
	4	15.45	− 8	−87	0.991	0.984
4		16.90	7	81	1.000	1.006
5		19.20	3	35	(0.979)	0.979)
6		22.06	4	43	1.008	1.005
7		27.15	2	15	1.012	1.004
	Mean[a]				1.000	0.998
	Mean deviation[a]				0.006	0.009
	N—C				1.200	1.178
	C—O				1.170	1.198
	N—O				2.370	2.376

[a] The ratios in parentheses have been omitted from the final averaging as it is felt that they are falsified by an error of visual measurement—see text for discussion.

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[11] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 180.

calculated radial distribution function in Fig. 1, where the heights of the lines are the appropriate products Z_iZ_j.

Cyanic Acid.—The photographs of cyanic acid extended out to $s = 22$, showing four measurable maxima and three minima. The general intensity pattern was in fact very similar to that of a linear symmetric triatomic molecule, the maxima falling off rapidly to sharp minima on the inside, but running into broad shoulders on the outside. These shoulders were not easy to measure reproducibly, and we have not reported their positions. Those of the sharper maxima and minima are given in Table II with the visually estimated intensities and the corrected intensities, C_k. The radial distribution function for cyanic acid (Fig. 1) was calculated by the modified method, and shows clearly the similarity between the acid and its methyl ester. The peak at 1.19 Å. is the unresolved N–C, C–O, and N–H group, while the peak at 2.35 Å. corresponds to the N–O distance. Because of this close correspondence, and since it is known for independent evidence that the free acid does exist in the iso-form,[2,12] curves H, I and J of Fig. 3 were calculated at once for the structures of the cyanate group which were in reasonable agreement with the photographs for the methyl ester, namely, $^1/_3$, $^1/_3$, $^1/_3$, $^2/_5$, $^1/_5$, $^2/_5$, and $^1/_5$, $^2/_5$, $^2/_5$, respectively. The N–H distance was taken to be 1.01 Å. and the angle α was assumed to be 125°. As was the case for the corresponding models of the ester (which bear the same letters), all three curves are in good qualitative agreement with the photographs, but again the model of J becomes equivalent to H when the scale is transformed to give the best average quantitative agreement. Again no distinction can be made between models H and I, and both are included in Table II. For final values of the distances in the cyanate group in cyanic acid we shall again choose the averages of the scale-adjusted distances in models H and I, giving for the distances: N–C = C–O = 1.19 ± 0.03 Å. and N–O = 2.38 ± 0.03 Å. These distances are included with the cyanic acid radial distribution curve in Fig. 1, again weighted with the appropriate Z_iZ_j values; the assumed hydrogen distances are also represented for completeness, but of course they cannot be determined.

TABLE II

CYANIC ACID

Max.	Min.	s	I_k	C_k	s_H/s	s_I/s
1		6.20	15	49	1.019	1.016
	2	9.82	−10	−61	0.981	0.975
2		11.27	5	35	1.020	1.013
	3	15.04	− 1	− 8	0.995	0.991
4		16.66	2	15	1.013	1.008
5		21.84	$^1/_2$	2	1.014	1.007
	Mean				1.007	1.002
	Mean deviation				0.013	0.013
	N–C				1.208	1.182
	C–O				1.178	1.202
	N–O				2.386	2.384

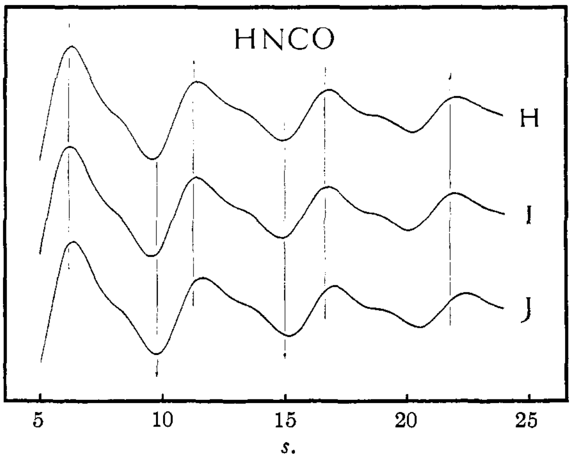
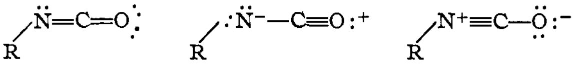


Fig. 3.—Theoretical intensity functions for models of cyanic acid; for information concerning the models see text. The arrows indicate measured maxima and minima.

Discussion

From these electron diffraction results, with the aid of the semiempirical relations of the Pauling type,[11,13] one may deduce the approximate contributions of the following three structures to the ground state of the covalent cyanate group



$R{-}\ddot{N}{=}C{=}\ddot{O}{:}$ $\quad$ $R{-}{:}\ddot{N}^{-}{-}C{\equiv}O{:}^{+}$ $\quad$ $R{-}N^{+}{\equiv}C{-}\ddot{O}{:}^{-}$

I II III

As has already been indicated, the experimental evidence shows that the actual contributions lie somewhere between $^1/_3$, $^1/_3$, $^1/_3$ and $^2/_5$, $^1/_5$, $^2/_5$; the final distances chosen for the cyanate group in methyl isocyanate correspond to 0.36, 0.26, 0.38. Although these ratios are strongly influenced by experimental errors, it is interesting to note that the structures which appear to be of the greater importance are those in which the atoms are either neutral or in which the formal

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[12] Goubeau, *Ber.*, **68**, 912 (1935).

[13] In this particular case the relations assume the following form:

$$N{-}C = (3.84\,x_{\text{I}} + 1.51\,x_{\text{II}} + 6.66\,x_{\text{III}})/(3x_{\text{I}} + x_{\text{II}} + 6x_{\text{III}})$$

$$C{-}O = (3.72\,x_{\text{I}} + 6.42\,x_{\text{II}} + 1.47\,x_{\text{III}})/(3x_{\text{I}} + 6x_{\text{II}} + x_{\text{III}})$$

charges are distributed in accordance with the relative electronegativities of nitrogen and oxygen, whereas the structure in which the formal charges are oppositely distributed may well contribute less. We feel that this is very probably a real effect, and that it constitutes a manifestation of another valence rule, which, through analogy with the formal charge rule, may be called the charge distribution rule. Further evidence of the existence of this rule will be mentioned presently. The fact that this observed structure of methyl isocyanate is very similar to that of methyl azide[9] is also in agreement with the known similarity of the infrared vibration spectra of these two compounds.[1a] Furthermore, a comparison of their Raman spectra tends even to confirm the observation that the distances in the cyanate group are much more nearly equal than are the analogous distances in the azide group, for while the only line characteristic of the cyanate group appearing in the Raman spectra of the alkyl esters of cyanic acid is the symmetric stretching frequency,[14] both the symmetric and antisymmetric frequencies appear with considerable intensity in methyl azide. The absence of the antisymmetric line in the Raman spectrum of a linear triatomic group suggests an approach to symmetry.

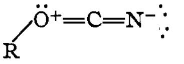
Goubeau[12] has shown that the crystalline cyanates may be divided into two classes on the basis of their Raman spectra. To the first group belong the cyanates of silver and mercury, whose Raman displacements are essentially identical with those of the isocyanate esters, except that a line corresponding to the asymmetric stretching frequency occurs weakly. To the second group belong potassium, lead, and tetramethylammonium cyanates, whose symmetric and antisymmetric frequencies both occur, but are considerably displaced toward lower frequencies. The former cyanates are probably nearly covalent, while the latter are undoubtedly ionic; hence it seems reasonable to seek to explain these differences in vibration frequencies through a differentiation between the structures of the covalently bonded cyanate group and the cyanate ion. The ground state of the ion is doubtlessly achieved through resonance among the following three structures

$$\vdots\bar{\mathrm{N}}{=}\mathrm{C}{=}\mathrm{O}\vdots \qquad {}^{-}{:}\,\underset{\cdot\cdot}{\ddot{\mathrm{N}}}{-}\mathrm{C}{\equiv}\mathrm{O}{:}^{+} \qquad {:}\,\mathrm{N}{\equiv}\mathrm{C}{-}\underset{\cdot\cdot}{\ddot{\mathrm{O}}}{:}^{-}$$

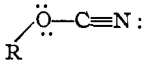
I II III

The lowering of the stretching frequencies and the increase in the asymmetry of the ion would be explained if the contribution of structure II, in which a positive formal charge is placed on the oxygen while a double negative formal charge is placed on the less electronegative nitrogen, were assumed to be very small. Complete resonance between structures I and III would then lead to a C–O distance of 1.30 Å. and a C–N distance of 1.21 Å., which would (by Badger's rule, for example) lead to a considerable weakening of the force constants with a resulting lowering of the frequencies, and would also destroy the approximate symmetry of the covalent group. Such an explanation might appear to be in disagreement with the known fact that the acid strengths of cyanic and hydrazoic acids are of the same order of magnitude, for it would mean that while a third resonating structure stabilizes the azide ion with respect to the un-ionized hydrazoic acid, the exact reverse would be the case with cyanic acid. This effect is, however, opposed by another effect, due to the fact that whereas the nitrogen atom in cyanic acid has a small positive formal charge, thus tending to repel the proton, the corresponding nitrogen atom in hydrazoic acid has one-half unit of negative formal charge tending to stabilize the un-ionized acid.

It appears to have been well established that both the cyanic acid itself and also in its alkyl esters, the attached group is linked through the nitrogen atom. In fact there seems to be no chemical evidence which demands the existence of the normal (oxygen-linked form) cyanic acid even as an intermediate in organic reactions,[15] though of course neither the diffraction nor the spectroscopic studies would rule out the existence of a small amount of the normal acid in equilibrium with the iso-acid. It is interesting to seek an explanation of the apparent instability of the normal cyanates with respect to the iso-compounds. The possible structures (involving five covalent bonds) for the normal cyanates are:



I



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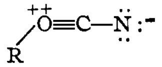

III

Now in neither structures I and III are the formal charges arranged according to the relative electronegativities of the oxygen and nitrogen

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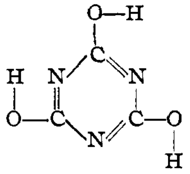
(14) Kopper and Pongratz, *Monatsh.*, **62**, 78 (1933).

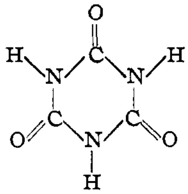
(15) Hückel, "Theoretische Grundlagen der organischen Chemie," Akademische Verlagsgesellschaft, Leipzig, Vol. I, 1931, p. 193.

atoms, and if we assume that these charge distributions, particularly in structure III, are so unfavorable that the contribution of structure I is somewhat smaller than that of structure II while that of structure III is almost negligible, the instability of the normal cyanates will be clear, for the resulting loss in resonance energy should be quite enough to make the normal cyanate unstable with respect to the isocyanate. Thus it becomes apparent that the observed structure of the isocyanate group, the indicated structure of the cyanate ion, and the apparent instability of normal cyanates may all be explained with the aid of a charge distribution rule. This rule may be tentatively enunciated as follows: all other things being equal, structures in which formal charges are not disposed in accordance with the relative electronegativities of the atoms will tend to contribute less to the ground state of normal molecules than will structures in which this is not the case, and this tendency will become rapidly more pronounced as the difference in electronegativities and the number of formal charges so disposed increase. This rule affords a ready understanding of the fact that both normal and iso-esters of thiocyanic acid are known, for with oxygen replaced by sulfur (which is slightly less electronegative than nitrogen) the analogs of structures I and III above will each be expected to contribute roughly a full third to the structure of the normal thiocyanates, so that the resonance energies of both the normal and the isothiocyanates should be approximately equal. Of course the situation is complicated by the possibility of resonance with structures in which the sulfur atom forms more than four covalent bonds.[16] The details of the structures of the thiocyanates may well be revealed by electron diffraction investigations now in progress in this Laboratory, so it seems premature to discuss the matter further here.

The polymerization of cyanic acid leads to a mixture of cyamelide, which is probably a linear polymer of fairly high molecular weight, and cyanuric acid, which is known to be a trimer containing the symmetrical triazine ring, in its normal form. An iso-form of the acid may also be written, and esters of both the normal and isocyanuric acid are known, but the former are converted into the latter on heating. This behavior may be explained, since the sum of the bond energies for the normal ester is 702 kcal., while that for the iso-ester is 756 kcal. The benzene-like resonance possible in the normal esters could hardly be expected to contribute more than 35–40 kcal., which is surely not enough to stabilize the normal esters with respect to the iso-esters. In the free acid one would expect the situation to be reversed, since the sum of bond energies for the normal acid is 832 kcal. while for the iso-acid the sum is 858 kcal. Here, then, the benzenoid resonance would actually stabilize the normal form of the acid. Apparently there is no conclusive chemical evidence on this point because the mobility of the hydrogen atoms is so great, and no direct physical measurements have been made on the acid which are capable of distinguishing the normal from the iso-form.



Cyanuric acid



Isocyanuric acid

The electron diffraction apparatus was constructed with the aid of generous grants from the Rackham Foundation and from the Midgley Foundation, which are gratefully acknowledged. One of us (E. H. E.) is pleased to acknowledge his special indebtedness to the National Research Council.

Summary

1. With the assumption of a tetrahedral methyl group with C′–H distances equal to 1.09 Å., the C′–N bond length as 1.47 Å., and a linear cyanate group, electron diffraction photographs of gaseous methyl isocyanate may be interpreted with the following structural parameters: N–C = 1.19 ± .03 Å., C–O = 1.18 ± .03 Å., N–O = 2.37 ± .03 Å., and an angle of 125° ± 5° between the linear cyanate group and the C′–N bond.

2. Similar treatment of photographs of cyanic acid vapor leads to the interatomic distances: N–C = 1.19 ± .03 Å., C–O = 1.19 ± .03 Å., and N–O = 2.38 ± .03 Å., with the N–H distance assumed equal to 1.01 Å., the cyanate group linear, and the angle between the linear cyanate group and the N–H bond equal to 125°.

3. It is shown that with the assumption of a

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(16) Reference 11, p. 210 ff.

simple and reasonable "charge distribution rule" not only these observed structures, but also other information concerning the cyanate ion and the chemistry of cyanic acid derivatives may be easily correlated with valence bond structures.

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 16, 1940

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dipole Moments of Alkyl and Phenyl Lead Halides

BY G. L. LEWIS, P. F. OESPER AND C. P. SMYTH

As part of a program of measurements of the dipole moments of molecules containing metallic atoms with the object of obtaining bond moments and studying their relation to the electronegativities of the bonded elements, the dipole moments of triphenyllead and of a number of methyl, ethyl and phenyl lead halides have been measured. The triphenyllead was given us by Professor Henry Gilman of Iowa State College, the several alkyl lead halides listed were given us by Dr. George Calingaert of the Ethyl Gasoline Corporation, and the three triphenyllead halides were given by Professor L. S. Foster of Brown University. The writers wish to express their gratitude for this assistance and wish further to thank Dr. Calingaert for advice on the purification of materials.

Purification of Materials

Benzene, for use as solvent, was purified as in previous work.[1] Because of the tendency of the lead compounds to decompose, it was necessary to purify most of them immediately before they were measured. The triphenyllead was twice precipitated from chloroform solution by addition of ethyl alcohol, being washed each time with petroleum ether. The crystals were placed in an evacuated desiccator and nine hours later dissolved to form clear benzene solutions, which were measured immediately. The alkyl lead halides were crystallized out of a warm petroleum ether–benzene solution, washed with a little petroleum ether, and dried in a stream of dry nitrogen. Everything was kept as close to 25° as possible so that the solutions could be made up and measured immediately at 25°. Several sets of measurements made before the development of this technique were discarded because of impurities in the materials as evidenced by high conductance and the development of opalescence in the solutions. The occasional appearance of a slight opalescence in some of the solutions finally used was insufficient to throw the results out of line with those in which no evidence of decomposition could be detected. The effects of the tendency to form an equilibrium mixture of the mono-, di-, trihalides, etc., although eliminated in part by the recrystallization of the materials, increased the probable errors in the results. The more stable triphenyllead halides were purified by recrystallization and measured in the usual manner.

Experimental Results

The dielectric constants were measured at a frequency of 520 kilocycles with a crystal-controlled heterodyne beat apparatus previously described,[2] and the densities were determined with an Ostwald–Sprengel pycnometer in a manner described previously.[3] The dielectric constants, ϵ, and the densities, d, of benzene solutions containing mole fraction, c_2, of the compound indicated are given in Table I, the polarizations P_2 being listed in the last column. The polarization of the pure benzene is given as P_1. The constants of the benzene used for the solutions of triphenyllead and the alkyl lead halides are given for $c_2 = 0$ under triphenyllead, while the slightly different constants of another lot of benzene used for the triphenyllead halide solutions are given under triphenyllead chloride. Table II lists in the second column the values of MR_D, the molar refraction for the D sodium line, calculated from the atomic refractions and the refraction of benzene given in Landolt–Börnstein, and the atomic refraction of lead 17.9 listed by Eisenlohr.[4] The third column gives the polarizations P_∞ obtained by extrapolation to $c_2 = 0$ of the values of P_2 in Table I, and the fourth column gives the dipole moments calculated in the usual manner. The probable errors in the moment values are unusually large because of the instability and low solubility of the substances, being approximately 0.1×10^{-18}, except in the cases of trimethyllead chloride and diethyllead dichloride, where they are 0.15×10^{-18}, because of the exceptionally low solubility of the former and of the greater than usual instability of the latter. Any errors introduced by calculation of the MR_D values are

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[1] Smyth and Walls, THIS JOURNAL, **54**, 1854 (1932).

[2] Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

[3] Lewis and Smyth, THIS JOURNAL, **61**, 3063 (1939).

[4] Eisenlohr, "Spektrochemie organischer Verbindungen," F. Enke, Stuttgart, 1912, p. 72.