Studies on Molecular Structure by the Measurement of the Dielectric Constants of Gases. III. The Dipole Moment and the Structure of Alkyl Nitrites

By Takehiko Chiba

(Received April 18, 1955)

Studies on molecular structure concerning the internal rotation have been made on many compounds such as ethane derivatives[1] but in these compounds both ends of internal axis have three atoms or groups which contribute to the forces determining the structure of these compounds. In alkyl nitrites both ends of the internal axis N-O have only an oxygen atom and a group R respectively, which will make the treatment easier. Recently Tarte made infrared investigation on alkyl nitrites[2] and found that there are two rotational isomers in these compounds.

This paper reports the results of the dipole moment measurement on some of the alkyl nitrites: ethyl, isopropyl, and tertiarybutyl nitrites in the gaseous state at various temperatures.

Preparation of the Materials

The samples were prepared by dropping concentrated hydrochloric acid in the mixture of corresponding alcohol and 35% aqueous solution of sodium nitrite in cooling. The raw products of the *i*-propyl and *t*-butyl nitrites seemed to decompose when washed with water; they were therefore first dried over calcium chloride and distilled, and then dry air was passed though them to exile the remaining NO and NO_2 gases, and finally redistilled. Ethyl nitrite was washed with sodium carbonate solution and distilled over calcium chloride. Ethyl nitrite b.p. 17°C, *i*-propyl nitrite b.p. 39.2–.4°C, *t*-butyl nitrite b.p. 63.0°C.

The Procedure and the Results of the Measurement

Because of the instability of the alkyl nitrites the measurement was made at temperatures below about 60°C. The electric part of the apparatus is that described in the previous paper[3], but some improvements were made on the thermostat, the gas cell, and the gas filling devices. A Dewar-vessel filled with insulating oil was used for the thermostat at low temperature (down to −20°C). Ethyl and propyl nitrites have vapor pressures high enough for the measurement of dielectric constant at these temperatures. The dimensions of the gas cell are the same as the cell "D" of the previous paper, but in order to keep the lead from contact with oil in the bath, a new cell was constructed which is shown in Fig. 1. To reduce the stray field the hot-side lead was covered with a nickel cylinder (A) of earth-side which itself formed a part of the earth lead. The part (A) was covered with a glass mantle (B) through which dry air was allowed to flow to avoid the condensation of moisture on it.

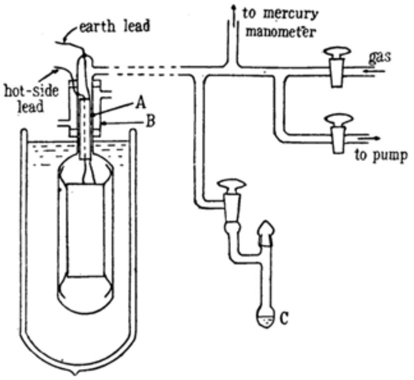


Fig. 1. Gas cell and vapor filling system.

The cell constant was calibrated many times by measuring the dielectric constant of carbon dioxide, and further checked with carbon tetrachloride and benzene. The correction due to the capacity of the part (A) was computed as a coaxial cylinder. Samples were introduced into the reservoir (C) by vacuum distillation. After each run of observations of $\Delta\epsilon$ and Δp, the cell was pumped out, and a fresh sample was used for each observation to avoid the errors due to the decomposition of the sample.

The results of the observations are summarized in Table I, Though these compounds are appreciably yellow colored, the extrapolation of the refractive index in visible region to infinite wave length shows no

---

[1] S. Mizushima, "Molecular Structure and Internal Rotation", (1954).

[2] P. Tarte, *J. Chem. Phys.*, 20, 1570 (1952).

[3] T. Chiba, This Bulletin, 28, 19 (1955).

TABLE I

OBSERVED POLARIZATIONS AND DIPOLE MOMENTS OF ETHYL, *i*-PROPYL AND *t*-BUTYL NITRITES

Ethyl nitrite

$P_E+P_A=1.05MR_D$(assumed)$=18.5$ cc.

T(°K)	n	p(mmHg)	P(cc.)	ΔP(cc.)	μ(D)
253.3	8	64–85	158.1	0.4	2.40_9
266.7	6	70–82	151.8	0.2	2.41_4
295.9	7	85–131	139.0	0.4	2.41_7
298.0	6	69–90	138.2	0.3	2.41_8
316.1	6	70–104	130.5	0.4	2.41_0
333.8	8	70–97	124.8	0.4	2.41_2

i-Propyl nitrite

$P_E+P_A=1.05MR_D$(assumed)$=23.3$ cc

T	n	p	P	ΔP	μ
256.1	7	33–52	181.6	0.6	2.57_8
267.4	8	25–56	174.9	0.3	2.57_8
284.2	7	46–63	164.7	0.5	2.56_8
300.3	8	51–74	157.2	0.2	2.56_8
314.3	8	54–70	151.2	0.5	2.56_8
332.4	7	56–83	143.8	0.4	2.56_2

t-Butyl nitrite

$P_E+P_A=1.05MR_D$(assumed)$=28.1$ cc.

T	n	p	P	ΔP	μ
288.8	5	45–51	183.2	0.6	2.71_1
291.0	6	41–63	181.1	0.7	2.70_1
301.4	4	51–63	175.1	0.4	2.69^5
313.2	5	65–77	169.2	0.4	2.69_1
330.1	5	57–67	161.2	0.3	2.68_4

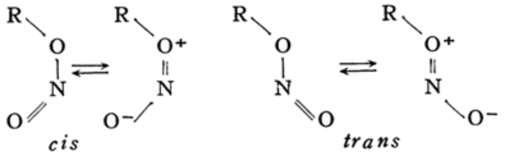
n: number of the observations.
p: pressure range of the observations.
ΔP: average deviation of P.

abnormality; for instance, for ethyl nitrite, $MR_D=17.60$ cc., $MR_\infty=17.32$ cc. (extrapolated), and a sum of atomic refractions $\Sigma AR_D=16.9$ cc. Therefore, P_E+P_A is taken as $1.05MR_D$ as in the usual cases.

The moment of ethyl nitrite in the gaseous phase was given by Czerlinsky⁴⁾ to be 2.38D at 17°C, and the dielectric constant of ethyl nitrite at 15°C and 760 mmHg given by Cordonier⁵⁾ is 1.0182, which corresponds to the dipole moment of 2.43D. The present results are in good agreement with these two.

Discussion

According to the infrared study of Tarte²⁾ the absorption lines assigned to $\nu_{N=O}$, ν_{N-O}, ν_{C-O}, and δ_{ONO} have doublet structure, the ratio of the intensity of each doublet line depending on alkyl radical, as well as on temperature. This phenomenon was explained adequately by the existence of the rotational isomers. It is, however, difficult to attribute the effect of giving two isomers to the forces such as steric or dipole one, since these forces should vary monotonously from the *cis* to the *trans* position. The possible explanation of this is to take into account resonances such as



which stabilizes the planar structure, i.e., the *trans* and the *cis*. A calculation of resonance energy was made by a simple MO method to estimate barrier height at 90°C position. This calculation was made for a four-electron system of the skeleton of $\text{-O}^{++}\text{-N}^{+}\text{-O}^{+}$ and for the corresponding localized system, and the potential barrier is taken as a difference in resonance energy between them. This was made after the procedure employed by Kurita and Kubo⁶⁾ for the case of tropolone except exchange integral β_{ij} between atoms i and j, i.e., β_{ij} was taken as $\beta_{ij}=\beta\cdot s_{ij}/s$, where β is an exchange integral of benzene π-electron, s_{ij} and s are corresponding overlap integrals. Bond distances used were those given by Rogowski⁷⁾ for methyl nitrite: that is N-O: 1.37Å, N=O: 1.22Å. From this calculation the barrier height of 0.34β can be obtained; therefore if we assume 30 kcal./mole for β, this barrier is as high as about 10 kcal./mole. This is only an approximate value, but as shown later, it is a reasonable order of magnitude compared with the case of HONO, and therefore, it can be said that the resonance force is large enough to separate these molecules into two isomers.

Since there is a small temperature dependence of the moments of *i*-propyl and *t*-butyl nitrite (see Table I), it must be concluded that an energy difference exists between the *cis* and the *trans* forms. The energy difference can be calculated by use of the well-known formula of the average moment $\bar{\mu}$ at the temperature T:

$$\bar{\mu}^2=\frac{\mu_c^2+\mu_t^2 s e^{\Delta E/RT}}{1+se^{\Delta E/RT}}, \tag{1}$$

where s denotes the ratio of the entropy factor of the *trans* form to that of the *cis* form. Its value cannot be computed since the curvatures at the potential minima are not known. Therefore, it is left as an un-

---

4) E. Czerlinsky, *Z. Physik*, 88, 515 (1934).

5) Cordonier and Guinchaut, *Compt. rend.*, 185, 1449 (1927).

6) Y. Kurita and M. Kubo, This Bulletin, 24, 13 (1951).

7) F. Rogowski, *Ber.*, 75B, 244 (1942).

known parameter which should be determined by the experiments.

Now, if the temperature dependence of the moment is small and $d\bar{\mu}/dT$ is constant in the range of the observation, then from Eq. (1) it is easily seen that

$$\Delta E = -2RT^2 \frac{(\mu_t^2-\mu_c^2)\bar{\mu}}{(\bar{\mu}^2-\mu_c^2)(\mu_t^2-\bar{\mu}^2)}\cdot\frac{d\bar{\mu}}{dT}. \qquad (2)$$

Thus the energy difference can be evaluated if we know the values of μ_c and μ_t without the knowledge of s. The value of s is calculated from Eq. (1), using the value of ΔE thus obtained[8].

The diple moments of the *cis* and the *trans* forms are calculated to be $\mu_c=1.27$D, and $\mu_t=2.97$D respectively, using $\mu_{\mathrm{N=O}}=2.0$D, $\mu_{\mathrm{N-O}}=0.3$D, $\mu_{\mathrm{R-O}}=1.1$D, and $\angle$RON = tetrahedral and $\angle$ONO$=120°$.[9] The values of ΔE and s which give the best fit with the observed temperature dependence of the dipole moments using μ_c and μ_t obtained above are given in Table II. As mentioned above, the contribution of the resonance forms is considerable in these molecules. Hence in calculating μ_c and μ_t it will be more reasonable to take into account the polar structures[10]. However, the simple MO calculation does not provide a reliable estimate to the augmentation of the moments, since it has usually a trend to give considerably high values. In Table II there are also shown the values obtained by assuming 10% higher values for μ_c and μ_t. It is seen from this table that, if we take higher values for μ_c and μ_t, ΔE's of *i*-propyl and *t*-butyl nitrites becomes smaller. Hence, although there are some ambiguities in the values of μ_c and μ_t, it can safely be said that ΔE of *i*-propyl nitrite is estimated to be less than about 140 cal., and that of *t*-butyl nitrite to be less than 340 cal. Thus ΔE increases in the order of methyl, ethyl, *i*-propyl and *t*-butyl nitrites, although ΔE is not great in the last two compounds.

Tarte[11] obtained ΔE from the measurements of the temperature dependence of the intensity of absorption lines assigned to both isomers. His result is -350 cal. for methyl nitrite and nearly equal to zero for ethyl and *i*-butyl nitrites, and $\Delta E \gg 0$ in *t*-butyl nitrite. In the last case accurate value was not obtained since the *cis* absorption line is very weak. The constant moment of ethyl nitrite in the present work agrees well with his result.

TABLE II

ΔE AND s VALUES OF ALKYL NITRITES ESTIMATED FROM THE OBSERVED DATA OF DIPOLE MOMENT

	$\mu_t=2.97$D, $\mu_c=1.27$D,		$\mu_c=1.40$D, $\mu_t=3.27$D.	
	s	ΔE cal./mol.	s	ΔE cal./mol.
CH_3ONO	1.5^a	(—350)	0.9^a	(-350)
C_2H_5ONO	1.4	0	0.8	0
$(CH_3)_2CHONO$	1.8	140	1.0	100
$(CH_3)_3CONO$	2.1	340	1.1	200

a: These values are estimated using dielectric constant data for methyl nitrite given by Cordonier (Ref. 5).

We shall next consider these ΔE values from the theoretical considerations. First of all, it should be mentioned that the resonance effect is not a main cause of the energy difference between the isomers because the effect of alkyl radical R on the resonance is that of a higher order. Therefore we have to look for the origin of the energy difference in some other effect. It is seen that the dipole-dipole interaction between R-O and O-N stabilizes the *cis* position whereas the steric force between the radical R and the end O atom has an opposite effect. Since dipole interaction energy does not vary so much by replacing R, the difference obtained for different radicals may be mainly due to the steric effect. It can easily be understood that ΔE of steric nature is higher in (Et......O) than in (Me......O) because in the former a hydrogen atom of a methyl radical is replaced by another methyl and, in the same way ΔE in (*i*-Propyl,......O) is higher than in (Et......O), and in (*t*-Butyl......O) higher than in (*i*-Propyl......O). If we replace one hydrogen atom of a methyl radical by another methyl or by other alkyl radical with longer chain, the steric energy may remain nearly

---

[8] ΔE is taken here to be positive when the *trans* form is more stable than the *cis* one.

[9] $\mu_{\mathrm{N=O}}=2.0$D was given by Smyth from the value 2.5D of *t*-nitrosobutyl (Smyth, *J. Am. Chem. Soc.*, 60, 183 (1938)). The moment of N=O bond presumably varies with the extent of resononce, but on account of the lack of other available data, the above value is tentatively used.

[10] There is a possibility of larger μ_c and μ_t in higher alkyl nitrites by induction effect.

[11] P. Tarte, unpublished.

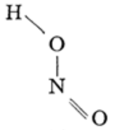
the same, because the atoms in the radical are far apart from the oxygen atom and the steric energy is probably determined by the interaction between the end oxygen atom and the atoms in α, β-position of R. Really a similar situation has already been found in ethane derivative hydrocarbons. The hindering barrier against the internal rotation around C-C axis in propane is considerably higher than that in ethane, but the difference does not increase so much in *n*-butane, or *n*-pentane[12]. By these considerations, the observed change in $\varDelta E$ by replacing R and the spectroscopic result of nearly equal $\varDelta E$ in ethyl and in *i*-butyl nitrite can be adequately explained.

A peculiar feature of the spectrum of alkyl nitrites is that the ratio of the extinction coefficients ($\ln I_t/\ln I_c$) of the $\nu_{N=O}$ band in the *cis* and the *trans* isomers is constant in esters of same α-carbon class of R, but differs appreciably in different classes[2]. Now the ratio of the extinction coefficients is given by a product of the ratio of the number of molecules N_t/N_c and the square of the ratio of the change of the dipole moments with the normal mode of vibration:

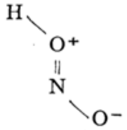
$$\ln I_t/\ln I_c=(N_t/N_c)|(d\mu/dQ)_t/(d\mu/dQ)_c|^2. \quad (3)$$

It is easily seen that the change of the ratio N_t/N_c is small, because it is given by the expression $s\cdot\exp(\varDelta E/RT)$ and the difference of $\varDelta E$ is small. Therefore the large change of the extinction coefficients must be attributed to a large change of the ratio $(d\mu/dQ)_t/(d\mu/dQ)_c$. However, from the ordinary concept of the normal vibration, such a large change cannot be expected at all, since the inner vibration of the N=O group is hardly affected by the structure of the outer part of that group. One explanation is the change of the amount of resonance, but this must bring about a considerable change of $\varDelta E$, contrary to the observed result. Thus the explanation of the above fact requires further study.

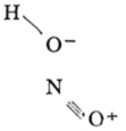
Lastly a few words should be added with regards to HONO molecule. This molecule is too unstable for the measurement of the dipole moment, but several authors reported the infrared spectrum. It is interesting to compare these results with those of RONO. According to the studies of Jones[13] and of D'Or[14] the characteristic frequencies of this molecule $\nu_{N=O}$, and ν_{N-O}, and δ_{ONO} have doublet structure, from which the molecule is considered to have also two rotational isomers, the *trans* and the *cis* forms. From the measurement of the temperature dependence of band intensity, Jones concluded that the *trans* form is about 500 cal. more stable than the *cis* form. This conclusion seems to be unlikely at first sight, since the steric force between O and H in the *cis* position is smaller than that between O and R. Actually, however, in the spectrum of HONO there are several points different from that of RONO; namely, $\nu_{N=O}$ of RONO is lower than that of HONO, on the contrary, ν_{N-O} of the former is higher than that of the latter. From these results, Jones suggested that in HONO the central N-O bond is much weaker than in RONO, which is a result of a contribution of the resonance form (III) besides (I) and (II).



(I)



(II)



(III)

The potential barrier of internal rotation of HONO is found to be 9–10 kcal., using the torsional frequencies given by these authors, and assuming the cosine type potential ($V=\frac{1}{2}V_0(1-\cos\varphi)$). In RONO this frequency is not observed, but it is very interesting to compare the value 9–10 kcal. of HONO with the value 10 kcal. of RONO derived from the MO calculation described earlier.

Summary

The dipole moment measurement was made at various temperatures on ethyl, *i*-propyl and *t*-butyl nitrites. Observed moments are 2.41D for ethyl, 2.57D for *i*-propyl, 2.70D for *t*-butyl nitrite at room temperature. The moment of the latter two compounds decrease slightly with temperature while ethyl compound remains constant. These esters are considered to consist of two isomers: the *trans* and the *cis* separated by a barrier of several kcal. due to a resonance effect. The energy difference $\varDelta E$ between the two isomers is found to be zero in ethyl, <140 cal. in *i*-propyl, and <340 cal. in *t*-butyl nitrite; in the latter two the trans from being more stable.

This change in $\varDelta E$ with replacing R is satisfactorily explained as due to the steric energy between R and the end oxygen atom.

---

[12] K. S. Pitzer, *Faraday Soc. Disc.*, **10**, 66 (1951); G. Herzberg, "Infrared and Raman Spectra", (1945), p. 520.

[13] I.H. Jones et al., *J. Chem. Phys.*, **19**, 1599 (1951).

[14] L. D'Or and P. Tarte, *Bull. soc. roy. sci. Liege*, **1951**, 478.

The author wishes to express his sincere thanks to Prof. Y. Morino and to Dr. Miyagawa for the kind guidance and valuable advice through this study and to Dr. P. Tarte of the University of Liège, who kindly informed the author of his spectroscopic results including some of the unpublished data. The cost of this research has been defrayed from the Grant in Aid for Fundamental Scientific Research from the Ministry of Education to which the author's thanks are also due.

Department of Chemistry, Faculty of
Science, Tokyo University,
Tokyo