

## THE CONFORMATION OF AROMATIC CARBAMATES IN SOLUTION: A DIPOLE MOMENT STUDY

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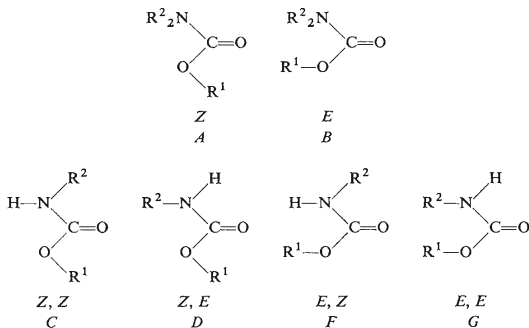
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Dipole moments of ten carbamates were measured in benzene solution and interpreted in terms of the conformation around the C—O and C—N bonds, taking the advantage of *para*-substituted derivatives and of cyclic model compounds. The  $n-\pi$  conjugation CO—N is manifested by a mesomeric moment whose contribution is, however, not decisive for the following conclusions. The conformation within the "ester" moiety of carbamates is uniformly *Z* and corresponds to that of other esters. Within the "amide" moiety the conformation depends more on substitution and solvent; however, in simple N-monosubstituted derivatives, like I—V, the *Z* form generally prevails. The most stable forms are thus *Z* (*A*) and *Z,Z* (*C*) for symmetrically or unsymmetrically substituted derivatives, respectively.

The conformation of N-substituted carbamates (urethanes) is of interest from two points of view. Firstly, the carbamate moiety enters as a protecting group the molecules of amino acids and peptides and must be dealt with when solving their conformation<sup>1</sup>. Secondly, the atomic groupings can be recognized within the carbamate molecule which occur separately in esters and N-substituted amides. Hence the question arises whether the typical conformations of the two classes of compounds are simply repeated in carbamates, or more or less changed. The problem thus consists in the conformation around two adjoining bonds and is related to a more particular problem<sup>2</sup> concerning two equivalent bonds in such a position. The solution would yield the partial answer to a more general question: to what extent the conformation of a complex molecule can be predicted on the basis of simpler ones?

Following the relation to esters and amides we may anticipate planarity of the whole functional group of carbamates, at least as a first approximation. Although the arrangement on nitrogen is not exactly planar in amides, the two substituents are, nevertheless, situated near the O=C—N plane<sup>3</sup>. The approximate planarity is corroborated in the case of carbamates by the values of rotational barriers around the C—N bond<sup>4,5</sup>. The barriers of rotation around the C—O bond is lower<sup>6</sup>, like in esters<sup>7</sup>, but the planar arrangement can be hardly doubted<sup>8</sup>. Accordingly, two forms (*A*, *B*) come into consideration for unsubstituted or symmetrically N,N-disubstituted carbamates and four forms (*C*—*G*) for N-monosubstituted carbamates.



As far as the analogy with esters and secondary amides were perfect, the *Z* forms (A and C) would be preferred throughout. This seems actually to be fulfilled in the crystalline phase for ethyl carbamate<sup>9</sup> and *N*-monosubstituted<sup>1,10</sup> or *N,N*-disubstituted<sup>11</sup> derivatives. On the other hand, the solution conformation is controversial. The recent NMR studies<sup>4,5</sup> dealt only with the rotation around the C—N bond in *N,N*-disubstituted derivatives and assumed\* the *Z* conformation in the ester moiety. The latter is based essentially on dipole moment measurements of simple derivatives in dioxan solution and on comparing with cyclic models<sup>14</sup>. It has, however, been recently questioned<sup>15</sup> and the dipole moment of ethyl carbamate interpreted in terms of the *E* ⇌ *Z* equilibrium within the ester moiety with *E* more populated. The main supporting argument was the doubled carbonyl band in the IR spectra<sup>15</sup>. On the other hand, the N—H band was found either doubled<sup>15,16</sup> (in CCl<sub>4</sub>) and interpreted by two conformations around the C—N bond<sup>16</sup>, or single<sup>17</sup> (in CHCl<sub>3</sub>) and assigned to the *Z* conformation on this bond. The latter authors formulated the conformation of the ester moiety as *E* without actual grounds<sup>17</sup>. The same criticism applies to other IR spectral studies<sup>18–20</sup> preferring either the *E* or the *Z* conformation.

The main cause of this confusion is clearly the fact that the conformations around the C—O and C—N bonds were not always distinguished. Although a complex approach is of course desirable, we felt that the dipole moment measurement could contribute significantly to the problem at its present stage. However, two conditions

\* The claimed *E* ⇌ *Z* equilibrium around the C—O bond of a complex carbamate<sup>12</sup> was later retracted<sup>13</sup>. Actually, it was the conformation around C—N which was subjected to change, and the chemical shift of the ester alkyl group was controlled by intramolecular shielding of a remote aromatic ring<sup>13</sup>.

must be fulfilled: both symmetrically and unsymmetrically substituted derivatives must be studied in order to separate the problems of conformation in the two moieties, and polar substituents in different positions must be introduced which allow to evaluate results from several compounds together by a graphical comparison<sup>21</sup>. Therefore, the compounds selected for the study (Table I) were mostly aromatic derivatives: aryl N,N-dimethylcarbamates VI–VIII, aryl N-methylcarbamates I–III, and methyl N-arylcarbamates IV, V. The remaining two cyclic model compounds IX, X were the same as in a previous dipole moment study<sup>14</sup>. In contradistinction to that work, the solubility of our compounds allowed to carry out all the measurements in benzene.

## EXPERIMENTAL

**Materials:** All compounds were prepared using procedures given in the literature. Phenyl N-methylcarbamate (I), m.p. 85–86°C, ref.<sup>22</sup>. 4-Chlorophenyl N-methylcarbamate (II), m.p. 115–116°C, ref.<sup>22</sup>. 4-Nitrophenyl carbamate (III), m.p. 159–161°C, ref.<sup>22</sup>. Methyl N-phenylcarbamate (IV), m.p. 47–48°C, ref.<sup>23</sup>. Methyl N-(4-chlorophenyl)carbamate (V), m.p. 116 to 118°C, ref.<sup>24</sup>. Phenyl N,N-dimethylcarbamate (VI), m.p. 44–45°C, ref.<sup>25</sup>. 1-Naphthyl N,N-dimethylcarbamate (VII), m.p. 54–55°C, ref.<sup>26</sup>. 4-Nitrophenyl N,N-dimethylcarbamate (VIII), m.p. 102–103°C, ref.<sup>27</sup>. 1-Oxa-3-aza-2-cyclopentanone (IX), m.p. 88–89°C, ref.<sup>28</sup>. 1-Oxa-3-aza-2-cyclohexanone (X), m.p. 83°C, ref.<sup>29</sup>.

**Physical measurements:** The dipole moments were determined by a standard procedure<sup>2,21</sup>. Dielectric constants and densities of benzene solutions (concentration range 0.005–0.05M) were measured at 25°C and the extrapolation carried out according to Halverstadt and Kumler<sup>30</sup>. Molar refractions were calculated from Vogel's increments<sup>21</sup> and additional increments (exaltations) for the conjugation O–C<sub>6</sub>H<sub>5</sub> (0.3 cm<sup>3</sup>) and NO<sub>2</sub>–C<sub>6</sub>H<sub>4</sub>–O (0.4 cm<sup>3</sup>); the exaltations for the conjugation NH–C<sub>6</sub>H<sub>5</sub>, N–C<sub>6</sub>H<sub>5</sub>, NO<sub>2</sub>–C<sub>6</sub>H<sub>4</sub>, Cl–C<sub>6</sub>H<sub>4</sub> are already included in the increments derived from aromatic derivatives. The increment for the 1-naphthyl group was derived from the molar refraction of 1-ethylnaphthalene<sup>32</sup>. The conjugation CO–NH is open to question; according to molar refraction data on N,N-dimethylamides<sup>33</sup> it seems that no exaltation is required. Correction for the atomic polarization was 5% or 15% of the R<sub>D</sub> value. All the results are listed in Table I.

**Calculations:** The dipole moments expected for the compounds I–X in different conformations were calculated according to the simple bond moment scheme with the standard values<sup>34</sup>: H–C<sub>ar</sub> 0.3 D, H–C<sub>ar</sub> 0 D, C–O 0.74 D, C=O 2.5 D, C–N 0.45 D, H–N 1.3 D, C<sub>ar</sub>–Cl 1.6 D, C<sub>ar</sub>–NO<sub>2</sub> 4.0 D. The mesomeric moment expressing the conjugation CO–N was adjusted according to the experimental dipole moment of 2-oxazolidinone (IX), see Discussion. No mesomeric moments were introduced for the conjugation O-Aryl or N-Aryl due to the supposed non-coplanarity of the benzene rings.

The valence angles used were average values from recent X-ray data<sup>1,9,11</sup>: ∠ O=C–O 122°, ∠ O=C–N 127°, ∠ C–O–C 115°, all the angles on N 120°. The geometry of 2-oxazolidinone was estimated on the basis of the following bond lengths, taken from the same sources<sup>1,9,11</sup>: (O) C–O 1.34 Å, (O) C–N 1.35 Å, C–O 1.43 Å, C–N 1.45 Å, C–C 1.54 Å. The least deviations from the above valency angles were obtained with the following angles in the planar five-membered cycle ∠ O–C–N 111°, ∠ C–O–C 112°, ∠ C–N–C 110°, ∠ O–C–C 103°, ∠ N–C–C 104°, ∠ O=C–O 122°, ∠ C–N–H 125°.

## RESULTS AND DISCUSSION

The calculated dipole moments are listed in Table I only for the actually assumed conformations, otherwise they are represented graphically in Figs 1–4. They involve the only point open to discussion, *i.e.* the contribution of the CO—N conjugation. The conjugation within the amide group is evident from the bond lengths and from other proofs<sup>3</sup>; within the framework of the bond moment scheme it may be expressed

TABLE I  
Polarization Data and Dipole Moments of Carbamates (Benzene, 25°C)

	Compound	$\alpha^a$ $\beta^a$	$P_D^0, \text{cm}^3$ $R_D^{20}, \text{cm}^3 b$	$\mu(5)^c, \text{D}$ $\mu(15)^c, \text{D}$	$\mu \text{ calc.}^d$
<i>I</i>	$\text{CH}_3\text{NHCOOC}_6\text{H}_5$	6.17 -0.286	239.7 41.1	3.10 3.07	2.95 (2.81) <sup>e</sup>
<i>II</i>	$\text{CH}_3\text{NHCOOC}_6\text{H}_4\text{Cl-4}$	10.75 -0.390	416.4 46.1	4.25 4.22	4.18 (4.09) <sup>e</sup>
<i>III</i>	$\text{CH}_3\text{NHCOOC}_6\text{H}_4\text{NO}_2\text{-4}$	20.8 -0.442	807.3 47.9	6.09 6.07	6.35 (6.30) <sup>e</sup>
<i>IV</i>	$\text{C}_6\text{H}_5\text{NHCOOCH}_3$	4.18 -0.285	157.4 41.9	2.35 2.32	2.86 (2.64) <sup>e</sup>
<i>V</i>	$4\text{-ClC}_6\text{H}_4\text{NHCOOCH}_3$	7.27 -0.387	295.4 46.8	3.47 3.44	3.85 (3.37) <sup>e</sup>
<i>VI</i>	$(\text{CH}_3)_2\text{NCOOC}_6\text{H}_5$	5.12 -0.252	205.0 46.0	2.76 2.72	2.41
<i>VII</i>	$(\text{CH}_3)_2\text{NCOOC}_{10}\text{H}_7(\alpha)$	4.03 -0.316	216.1 63.7	2.70 2.64	2.41
<i>VIII</i>	$(\text{CH}_3)_2\text{NCOOC}_6\text{H}_4\text{NO}_2\text{-4}$	19.6 -0.405	820 52.7	6.11 6.09	5.96
<i>IX</i>	$\text{NHCOO}(\text{CH}_2)_2$	16.14 -0.460	281.6 18.9	3.58 <sup>f</sup> 3.56	3.56
<i>X</i>	$\text{NHCOO}(\text{CH}_2)_3$	14.9 -0.446	304.0 23.6	3.69 <sup>f</sup> 3.68	—
—	$\text{NH}_2\text{COOC}_2\text{H}_5$	—	—	2.59 <sup>g</sup>	2.62
—	$(\text{CH}_3)_2\text{NCOOCH}_3$	—	—	2.59 <sup>h</sup>	2.20

<sup>a</sup> Slopes of the Halverstadt-Kumler plots<sup>30</sup>  $\epsilon_{12}$  vs  $w_2$  and  $d_{12}^{-1}$  vs  $w_2$ , respectively; <sup>b</sup> calculated from increments as given in Experimental; <sup>c</sup> with the correction for atomic polarization, 5% or 15% of the  $R_D$  value, respectively; <sup>d</sup> calculated for the conformations *Z* (*A*) or *Z,Z* (*C*) with the mesomeric dipole moments of 0.3 D in the directions of both the N—C and C=O bonds, see Experimental for the details; <sup>e</sup> for the mixture of the *Z,Z* (*C*) and *Z,E* (*D*) forms; <sup>f</sup> the dipole moments of 5.07 and 5.10 D for *IX* and *X*, resp. were found in dioxan<sup>14</sup>; <sup>g</sup> ref.<sup>14</sup>; <sup>h</sup> ref.<sup>15</sup>.

by formally different means and evaluated to differing figures<sup>35,36</sup>. Previously we used the expression by two vectors of 0.45 D in the directions of the bonds C=O and N—C, respectively<sup>36</sup>, for compounds of somewhat different structure than ours. Hence our first task was to verify these mesomeric moments and also the remaining bond moments, referring to the rigid molecule of 2-oxazolidinone (*IX*). The assumption of its planarity is reasonable and small deviations cannot affect the results.

FIG. 1

Comparison of Squared Dipole Moments of N,N-Dimethylcarbamates *VI* (x-axis) and *VIII* (y-axis)

Full points — values calculated for the *E* and *Z* conformation, hatched circle — experimental values.

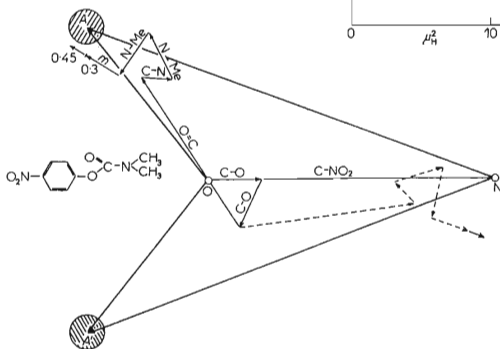
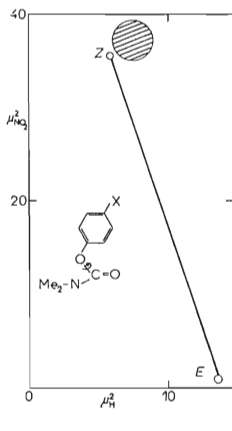


FIG. 2

Analysis of Dipole Moments of N,N-Dimethylcarbamates *VI* and *VIII* into Components  
Direction of the experimental dipole moments (heavy arrows) has been determined by solving the triangle *DNA*. The component vectors are shown for the actual *Z*-conformation (light arrows) and for the alternative *E*-conformation (broken arrows).

With the geometry described in Experimental we obtained the expected dipole moments of 3.46 or 4.27 D with and without the mesomeric correction, respectively. Our model compound would thus require somewhat smaller mesomeric corrections, say 0.15 D, but, with respect to previous<sup>36</sup> and following results, we used an intermediate value of 0.30 D for all the compounds under study. It will be shown that the exact value of this increment is not important for the conclusions to be achieved.

With the latter value we calculated the expected dipole moments for the N,N-dimethylcarbamates *VI* and *VIII* and compared with experiment in Fig. 1. The decision is conclusive. No trace of the *E* form can be detected within the limits of accuracy; if only the pure forms *Z* and *E* are considered, the decision is so reliable that it cannot be expressed by any probability. In order to estimate the significance of individual bond moments, in particular of the mesomeric contribution, we carried out the analysis into components (Fig. 2). Of decisive importance is the C=O bond moment, its raising would clearly improve the calculated result. If its well-tryed value of 2.5 D is to be maintained, a mesomeric correction is necessary and the two

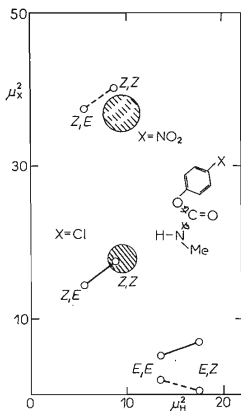


FIG. 3

Comparison of Squared Dipole Moments of N-Monomethylcarbamates *I* (*x*-axis), *II* and *III* (*y*-axis)

Full points — values calculated for the conformations *ZZ*, *ZE*, *EZ*, and *EE*; hatched circles — experimental values.

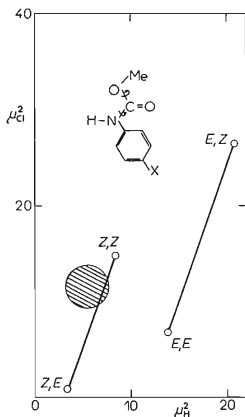


FIG. 4

Comparison of Squared Dipole Moments of N-Aryl Carbamates *IV* (*x*-axis) and *V* (*y*-axis)

See Fig. 3 for details.

vectors of 0.3 D each are of reasonable magnitude. It is also evident that this correction does not in the least influence the decision concerning conformation. A possible deviation from planarity on nitrogen (say up to  $30^\circ$ ) would affect only the two N—CH<sub>3</sub> bond moments and would not influence this decision either. No rotation of the N(CH<sub>3</sub>)<sub>2</sub> group around the C—N bond is manifested at all in the dipole moments, as far as this group is planar.

When proceeding to N-monosubstituted carbamates, we got the results shown in Figs 3 and 4. Again the *Z* conformation within the ester moiety is the only possibility in both cases. As to the conformation within the amide grouping, the results are not so unambiguous. In the case of N-methyl derivatives (Fig. 3) the *Z* form complies well with the experimental results but the difference between the two forms is small so that the presence of some *E* form in equilibrium cannot be excluded. A deviation from planarity on nitrogen would be without significance for the results. In the case of N-aryl derivatives (Fig. 4) a mixture of the two forms is indicated, in the ratio *Z* : *E* c. 3 : 1. A possible distortion of the planar arrangement could be of more importance but it is just in this case quite improbable due to the conjugation with the aryl group.

When generalizing our results and comparing with the previous ones, we must discuss separately the conformations in the two moieties. The *Z* conformation around the C—O bond is in our opinion quite general and as firmly established as any conformation in solution may be. It has been already deduced in a previous dipole moment study<sup>14</sup> which yielded the values of 2.59 and 2.64 D for two alkyl carbamates unsubstituted on nitrogen; with our set of bond moments we would calculate 2.62 and 4.46 D for the *Z* and *E* conformations, respectively. The *Z* conformation agrees also with the available X-ray data<sup>1,9,11</sup> and it fits also into the general picture of a uniform conformation of all esters.\* The only contradictory claim<sup>15</sup> is based on some misinterpreted facts and not well founded assumptions.

Oki and Nakanishi<sup>15</sup> interpreted the experimental dipole moment of methyl N,N-dimethylcarbamate (2.59 D) in terms of an equilibrium of the *Z* and *E* forms for which they calculated 1.38 and 3.48 D, respectively. However, the values calculated with our bond moments are 2.20 and 3.99 D and suggest merely the *Z* form. The example shows the danger of drawing conclusions from a single dipole moment value without referring to derivatives and model compounds. The temperature dependence of the dipole moment<sup>15</sup> is within the limits of experimental error and, in addition, may be caused by solvent effect. The most important experimental finding was the doubled band of the carbonyl stretching vibration in the IR spectra of carbamates of all types<sup>15</sup> but there is no proof that it is due to a conformation difference, in particular the temperature dependence has not been examined. The doubled N—H bonds<sup>15</sup> agree with previous findings<sup>16</sup> and are more probably connected with the conformation around the C—N bond<sup>16</sup>. Oki and

\* Only with tert-butyl formate in polar solvents the *E* form was detected in equilibrium<sup>37</sup>. With this exception all esters are in the *Z* conformation under all conditions<sup>8</sup>, some contradictory statements have been recently disproved<sup>13,38</sup>.

Nakanishi assume that this conformation must be *Z* as usual in secondary amides, hence any change of conformation must concern the C—O bond<sup>15</sup>. This reasoning is unsound since just a reverse one, referring to esters, would be even more appropriate. Oki and Nakanishi investigated several other ester-like compounds by the same approach and came to similar conclusions<sup>39–41</sup> at variance with most previous findings. Some of these conclusions have been since clearly disproved<sup>38,42</sup> and it is probable that all these papers<sup>15,39–41</sup> are essentially in error.

Concerning the conformation around the C—N bond of carbamates, we must state that it is less rigid and may depend more on substitution and solvent than that around the C—O bond. This result could be anticipated as it reflects the principal difference between the uniform conformation of esters<sup>8</sup> and the much more variable conformation of amides<sup>43</sup>. According to our results both amide conformations may be present in *N*-monosubstituted carbamates with the *Z* form always prevailing. This finding agrees with the X-ray<sup>1</sup> and IR spectroscopic<sup>16,17</sup> results, some disagreement as to the ratio of rotamers<sup>16,17</sup> may be due to different solvents; the dipole moments method is insufficiently sensitive to determine this ratio unless a polar substituent is present, like in *V*. In practice it is thus possible to study successfully only the *N*-aryl derivatives and the results cannot be transferred to other substituents. The *N*-alkyl derivatives would be more suitable for the <sup>1</sup>H and <sup>13</sup>C-NMR spectroscopies<sup>44,45</sup>. The conformation of *O*-alkyl carbamates is of particular interest in connection with *N*-protected amino acids and peptides since practically all urethane protecting groups in use are *O*-benzyl or *O*-tert-butyl derivatives<sup>46</sup>. Although their conformation may be influenced by intramolecular hydrogen bonds<sup>44,45</sup>, the general preference of the *Z* form does not seem to be impaired.

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