

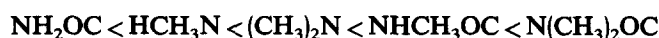
# Calculations of induced moments in large molecules. V.<sup>a)</sup> A study of intermolecular interactions and a functional group analysis of some amides, through the investigation of their polarizabilities and hyperpolarizabilities. A comparative study

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The calculated polarizabilities  $\alpha$  and hyperpolarizabilities  $\gamma$  of some amides are reported. The effect on these properties of methylation, bonding and nonbonding interactions, and isomerism has been analyzed. Some aggregates of formamide have been considered and the cooperative character of the intermolecular interactions is demonstrated. The effective properties ( $\alpha$  and  $\gamma$ ) of several functional groups, associated with the examined amides, were studied using an appropriate index. The established order for the relative polarizabilities of the considered functional groups is:



while the relative hyperpolarizabilities follow the order:



The computations have been performed by employing the CHF-PT-EB-CNDO method. This procedure gave, for the considered amides, polarizability values which are in satisfactory agreement with experimental data (theoretical and experimental values differ on average by 9.4%).

## I. INTRODUCTION

The electric properties of molecules and, in particular, their hyperpolarizability is an area of current research.<sup>1,2</sup> However, theoretical studies concerning hyperpolarizabilities of large molecules encounter severe difficulties<sup>3</sup> and thus computationally determined hyperpolarizabilities are relatively few. In this series of articles we consider various aspects of the structure-polarization relationship employing as probes terms in the expansion of the induced dipole moment.<sup>3-5</sup>

The objectives of this communication are:

(i) To present the static electric polarizability,  $\alpha$ , and second hyperpolarizability,  $\gamma$ , Ref. 6, of some amides: This class of compounds presents considerable theoretical and experimental interest because they are the simplest systems that exhibit peptide bonding.<sup>7</sup> Furthermore, this, to the best of our knowledge, is the first determination (experimental or theoretical) of their  $\gamma$ . Questions associated with substituent effects, the influence of bonding and nonbonding interactions, and the effect of isomerism on both  $\alpha$  and  $\gamma$  are discussed and analyzed.

(ii) To study the intermolecular interactions of some formamide aggregates: The ability of amides to form hydrogen bonds, (N-H ··· O=C) is of fundamental importance (e.g., in determining the structure of important naturally occurring molecules containing this group<sup>8</sup>). On the other hand the significance of polarization phenomena in the understanding of H-bonded systems is well documented,<sup>9</sup> while there are aspects, like the effect of environmental interactions arising

from such bonding on the molecular hyperpolarizability, which have received very little theoretical attention.

(iii) To report the relative polarizabilities and second hyperpolarizabilities of the functional groups:  $\text{NH}_2\text{OC}$ ,  $\text{NHCH}_3\text{OC}$ ,  $\text{N}(\text{CH}_3)_2\text{OC}$ ,  $\text{CH}_3\text{HN}$ , and  $(\text{CH}_3)_2\text{N}$ : The analysis of the relative properties of the more significant fragments of the examined amides contributes to the understanding of their induced moments, while the employed index<sup>5</sup> provides a measure of the effect of intramolecular interactions. The established orderings of the effective polarizabilities and hyperpolarizabilities allow a comparison with other functional groups.<sup>5</sup> Further, these are expected to be of importance in studies of substituent effects and in particular for approaches which use arguments based on polarization phenomena.<sup>5,10-12</sup>

This study has been performed by employing our CHF-PT-EB-CNDO method.<sup>2-5,13-16</sup> For isolated systems this method has been remarkably successful.<sup>2a, 13-15</sup> However, it is known that some CNDO-type procedures fail in certain cases related to interacting systems, for example in the calculation of stabilization energies.<sup>17</sup> Therefore, considerable care has been taken to ensure the reliability of our analysis by using basis functions optimized with respect to the known polarizability of amides, and normalized property values.

## II. COMPUTATIONAL METHOD

### A. Definition and justification of the model

The computations of  $\alpha$  and  $\gamma$  have been performed by the CHF-PT-EB-CNDO method. This approach relies on:

(a) a CNDO<sup>18</sup> wave function formed from a properly optimized basis set and

<sup>a)</sup>The preceding article in this series, Ref. 5, should have IV defined in its title.

(b) a self-consistent perturbation theory, that was developed by McWeeny and his co-workers, and which applies directly to the Fock-Dirac density matrix.<sup>19</sup>

The choice of the basis set is of central importance in our approach. Considerable computational experimentation has been carried out with orbitals of *s*, *p*, *d*, and *f* symmetries and many different exponents.<sup>14</sup> Analysis of these data has shown that high *l* AOs like *f* orbitals for carbon and *d* orbitals for hydrogen are sufficient (they can lead to reasonable results) but not necessary within a semiempirical framework, in particular if one takes advantage of the flexibility and freedom allowed within such schemes.<sup>14</sup>

It has been established that careful optimization of the exponents of a slightly extended basis set (usually involving *2s*, *2p* functions on second row elements and *1s*, *2s*, *2p* for H) provides, in general, the right computational apparatus for a physically sound description of the various orders of polarization.<sup>2a, 13-15</sup>

Further, our model, like other semiempirical methods,<sup>20</sup> contains (at least to some extent) a built-in allowance for electron correlation through the calibration of the basis set employing some judiciously chosen experimental results.

Overall it is considered that the reliability of the CHF-PT-EB-CNDO method, which has been carefully tested and confirmed in a wide variety of compounds and the essentially comparative character of the present study, ensure the validity of the proposed findings.

## B. Optimization of the basis set

We have already demonstrated that it is useful (both physically and computationally, since considerable savings are achieved) to employ basis sets, at least as a starting point, appropriate for the description of suitably chosen molecular fragments in order to develop functions applicable for the study of large systems.<sup>21</sup> This finding led to a scheme for the optimization of the basis set used to obtain the values for  $\alpha$  and  $\gamma$  of the following amides: formamide (FA), acetamide (AC), *N*-methylformamide (NMF), *N*-methylacetamide (NMA), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA).

The procedure was:

(i) The methyl group orbitals, which were successful for the calculation of  $\alpha$  and  $\gamma$  in a series of alkanes,<sup>13</sup> are used:

C:  $2s(1.625)$ ,  $2p(1.625)$ ,

H:  $1s(1.0)$ ,  $2s(0.5)$ ,  $2p(0.5)$ .

For the  $\text{NH}_x$  group ( $x = 1, 2$ ) the orbitals optimized with respect to  $\alpha$  and  $\gamma$  of ammonia (where the experiment gives 15.0 a.u.<sup>22</sup> and 6090 a.u.<sup>23</sup>, respectively, while the computed values are  $\alpha = 15.2$  a.u. and  $\gamma = 6060$  a.u.) have been employed. These are:

H:  $1s(0.8)$ ,  $2s(0.355)$ ,  $2p(0.355)$ ,

N:  $2s(1.875)$ ,  $2p(1.875)$ .

The same orbitals (exponents) have been used for  $\text{NH}_x$  in the amide and amine functional groups.

(ii) The orbitals of the C=O group of DMA were optimized with respect to its  $\alpha$ .

(iii) This basis set was used to compute the  $\alpha$  of AC and NMA. The steps (ii) and (iii) were repeated until the achieved agreement between theoretical and experimental values was considered satisfactory.

(iv) Employing the above defined C=O orbitals the functions of the aldehyde H were varied to approximate as closely as possible the polarizability of FA.

(v) This basis was used to calculate  $\alpha$  of NMF and DMF. The above process (ii)  $\rightarrow$  (v) was repeated until the experimental polarizabilities approached the calculated ones.

The resultant basis set contains the following orbitals:

C:  $2s(1.625)$ ,  $2p(1.625)$ ,

O:  $2s(2.4)$ ,  $2p(2.4)$ ,

H (bonded to CO):  $1s(0.9)$ ,  $2s(0.45)$ ,  $2p(0.45)$ .

This set of functions gave polarizability values for the considered amides, which differ, on average, from the experimental values by 9.4% (Table I). This observation and the fact that the employed computational procedure has given reasonably accurate polarizability and hyperpolarizability values for a wide variety of compounds<sup>13-15</sup> suggest that the hyperpolarizability values of the examined amides are sufficiently accurate to safeguard the validity of the reported comparative study.

## C. The convergence criteria

A detailed discussion on this matter has been given in Ref. 5. In summary the SCF was considered converged when the density matrix elements differed by less than  $10^{-4}$  and for the properties, by less than  $10^{-6}N$  (where  $N$  is the matrix order).

## III. RESULTS AND DISCUSSION

### A. The isolated molecules

The results of Tables I and II show that methylation leads to an increase in  $\bar{\alpha}$  which passes through a maximum while  $\bar{\gamma}$  uniformly increases and it is observed that the effect of substituting H by  $\text{CH}_3$  for the examined cases increases with the molecular weight of the compound. Similar trends occur for N and C methylation. We also observe that the effect of adding a net  $\text{CH}_2$  group is considerably larger than the property value of this entity in isolation ( $\gamma \cong 2000$  a.u.<sup>3</sup>).

A question of considerable importance is the contribution of bonding and nonbonding interactions to the molecular properties  $\alpha$  and  $\gamma$ . An index of these contributions is the difference between the additive value (considering the molecular property as a sum of the properties of the atoms which constitute the molecule, Table III) and the one which is produced by computation or experiment performed on the molecule as a whole (Table I). This quantity also gives a measure of the deformation in charge densities when atoms unite and form chemical bonds.

From the results of Table I we observe that the additive value for polarizabilities differs considerably from the experimentally determined values. The data for the second hyperpolarizability show that for two cases the difference

TABLE I. The polarizability  $\alpha$  and hyperpolarizability  $\gamma$  of some amides (the values are reported in a.u.<sup>a</sup>).

No.	Molecule <sup>b</sup>	$\alpha$			$\gamma$	
		Theory <sup>c</sup>	Additivity <sup>d</sup>	Experiment	Theory <sup>c</sup>	Additivity <sup>d</sup>
1	FA	23.1	38.3	27.5	8 270	7.360
2	AC	38.7	59.3	38.3	11 200	12 400
3	NMF	39.4	59.3	39.9	10 400	12 400
4	NMA	58.0	80.3	52.8	12 200	17 400
5	DMF	59.2	80.3	52.7	16 500	17 400
6	DMA	75.6	101	65.0	18 800	22 400

<sup>a</sup> 1 a.u. of polarizability  $\approx 0.148\ 176 \times 10^{-24}$  esu  $\approx 0.164\ 867 \times 10^{-40}$  C<sup>2</sup> m<sup>2</sup> J<sup>-1</sup>; 1 a.u. of hyperpolarizability  $\approx 0.503\ 717 \times 10^{-39}$  esu  $\approx 0.623\ 597 \times 10^{-64}$  C<sup>4</sup> m<sup>4</sup> J<sup>-3</sup>.

<sup>b</sup> For the molecular geometries, data have been collected from the following sources: 1:[29], 2:[30], 3:[30], 4:[30], 5:[31], 6:[31]. The coordinates of all molecules are available on request.

<sup>c</sup> Values determined by employing the CHF-PT-EB-CNDO method.

<sup>d</sup> Values formed from the sum of the atomic properties (Table III).

between the additivity and the computationally determined values are not large.

The various isomers of a molecule are usually studied in terms of their relative stability. We address a complementary question: How isomerism affects the ability of a species to respond to an external perturbation (which may be due to its intermolecular environment)?

We consider the pairs of isomers AC, NMF and NMA, DMF. In each pair the difference in  $\alpha$  is negligible. In the first pair the difference in  $\gamma$  is small while in the second it is considerable. Presumably this is due to the cooperative nature of adding a second methyl group to the nitrogen. It is useful to note that although in the examined cases the effect of isomerism on  $\alpha$  is negligible, other situations have been reported,<sup>14,15</sup> in which the difference is considerable.

## B. Intermolecular interactions

Semiempirical MO theories have provided useful information for H-bonded systems besides their well documented deficiencies.<sup>17,24,25</sup> In particular for large systems where elaborate *ab initio* methods are not considered applicable, well tested approximate methods are of real value.

TABLE II. Effect of adding methyl groups on the properties of formamide (the reported values are in a.u.).

No.	Molecule	$\bar{\alpha}^a$	$\Delta\alpha^b$	$\bar{\gamma}^a$	$\Delta\gamma^b$
1	FA	23.1		8 270	
			15.9		2530
2	AC, NMF	39.0		10 800	
			19.6		3550
3	NMA, DMF	58.6		14 300	
			17.0		4550
4	DMA	75.6		18 800	

<sup>a</sup> In cases where there are two isomers,  $I_1$  and  $I_2$  (e.g., AC and NMF), then  $\bar{\alpha}$  ( $\bar{\gamma}$ ) =  $[P(I_1) + P(I_2)]/2$ .

<sup>b</sup>  $\Delta P$  (where  $P$  is  $\alpha$  or  $\gamma$ ) is defined by the absolute value of the difference between two subsequent entries,  $\bar{P}_1$  and  $\bar{P}_2$  of Table I (e.g., 15.9 a.u. =  $|\bar{\alpha}(\text{FA}) - \bar{\alpha}(\text{AC, NMF})|$ ).

The reliability of our analysis is further safeguarded because:

(i) It is known that an accurate description of intermolecular interactions depends mainly on the outer parts of the molecules. Optimization of the wave function with respect to the polarizabilities of the isolated molecules helps to ensure the physically correct description of these outer regions of the charge cloud which will be influenced by such intermolecular interactions.

(ii) The interacting systems are probed using normalized values and thus the effect of possible systematic errors is reduced.

We have computed the properties of some linear multimers of formamide (Figs. 1 and 3). The results for these aggregates clearly show (Table IV) that their intermolecular interactions constitute a *cooperative process* (that is each interaction enhances the next one). Previous studies of these systems have shown that the energy per H-bond increases with the chain length. However the present results (Table IV) demonstrate that  $\alpha$  and  $\gamma$  are more powerful probes of changes induced in the molecular structure (e.g., redistribution of electron densities or charge transferred from one molecule to the other by association<sup>24</sup>).

The present results clearly show the effect of intermolecular interactions (in particular those which are developed between H-bonded systems) on molecular properties. The influence of these interactions on the electric nonlinearities has also been demonstrated experimentally.<sup>26</sup>

The results on the multimers of formamide and in particular the cooperative character of the interactions, may be

TABLE III. The polarizability  $\alpha$  (in a.u.) and second hyperpolarizability  $\gamma$  (in a.u.) of some atoms.

Atom	$\alpha$	$\gamma$
H	4.5 Ref. 32	1330 Ref. 34
C	12.0 Ref. 33	2350 Ref. 33
N	7.6 Ref. 33	630 Ref. 33
O	5.2 Ref. 33	389 Ref. 33

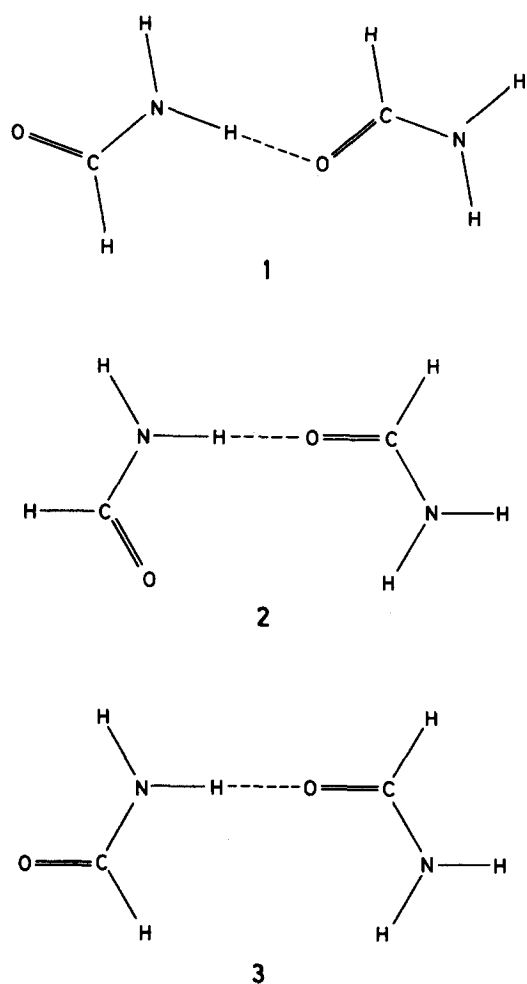


FIG. 1. Structure of some dimers considered in this paper.

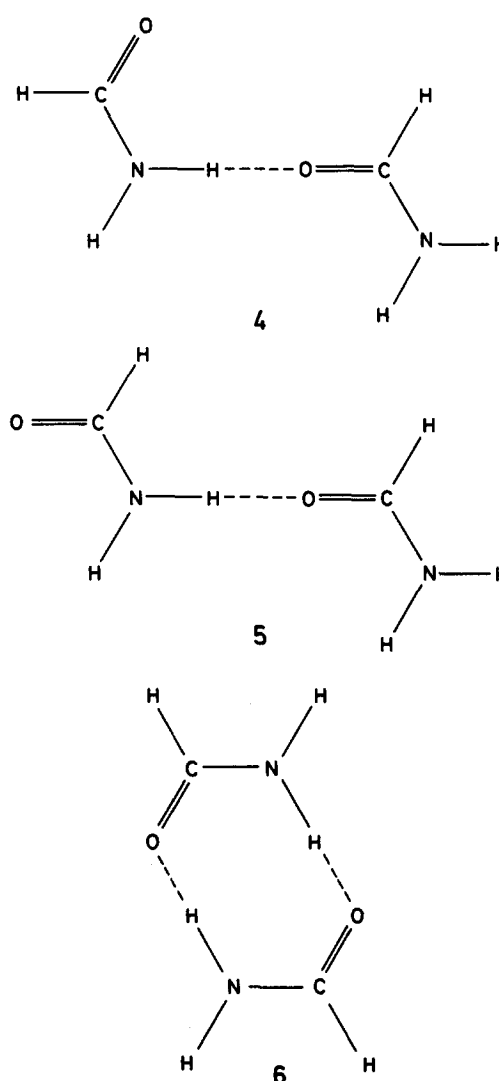


FIG. 2. Structure of some dimers considered in this paper.

rationalized by invoking the mutual polarization of the various parts (bonds, segments, etc.) of the system.

We have performed computations on various configurations of dimeric formamide (Figs. 1 and 2) in order to comment on the effect of the shape of the aggregate on its electric properties. We observe the differential effect which a change

in configuration has. Thus the following sequences result (Table V, Figs. 1 and 2):

$$\begin{aligned} \text{polarizability} &: 6 < 1 < 3 < 5 < 2 = 4, \\ \text{hyperpolarizability} &: 1 < 6 < 5 < 3 < 2 < 4. \end{aligned}$$

TABLE IV. Normalized polarizabilities and hyperpolarizabilities of some multimers of formamide. For comparison, the interaction energy and the energy per H bond reported by Hinton and Harpool (Ref. 7) are also quoted.

Multimer <sup>c</sup>	Normalized polarizabilities <sup>a,b</sup>	Normalized hyperpolarizabilities <sup>a,b</sup>	Interaction energy, kcal Ref. 7	Energy per H bond kcal Ref.7
(FA) <sub>2</sub> <sup>d</sup>	1.0 (1.0)	1.0 (1.0)	8.28	8.28
(FA) <sub>3</sub> <sup>e</sup>	2.1 (1.5)	2.1 (1.5)	18.49	9.25
(FA) <sub>4</sub> <sup>e</sup>	3.8 (2.0)	3.6 (2.0)	30.00	10.00

<sup>a</sup> The normalization has been performed with respect to the relevant properties of the formamide dimer.

<sup>b</sup> In parentheses are the numbers which would be found if there was not any interaction between the formamide molecules.

<sup>c</sup> The geometry of the monomer is from Ref. 29, while the O...H distance is from Ref. 35.

<sup>e</sup> The structure is given by No. 1 of Fig. 1.

<sup>d</sup> Figure 3.

TABLE V. Normalized polarizabilities and hyperpolarizabilities of some dimeric formamide conformers.

Configuration of (FA) <sub>2</sub> <sup>a</sup>	Normalized polarizabilities	Normalized hyperpolarizabilities
1	1.0	1.0
2	1.10	1.16
3	1.04	1.09
4	1.10	1.20
5	1.05	1.08
6	0.96	1.03

<sup>a</sup> Figures 1 and 2.

The pairs 2, 3, and 4, 5 illustrate the effect of rotating the CHO around the C–N bond. It is observed that 3 and 5 have lower polarizabilities and hyperpolarizabilities than 2 and 4, respectively. This phenomenon may partially be attributed to electrostatic interactions between the oxygen of C = O and the hydrogen of the N–H (which does not participate in an H bond).

### C. The effective polarizabilities and hyperpolarizabilities of the amide and some *N*-substituted groups with respect to hydrogen

The following relative property measure

$$P' = \frac{P(\text{XY})}{P(\text{HY})} - 1,$$

where  $P$  is either  $\alpha$  or  $\gamma$ , has been defined for the study of functional groups (NH<sub>2</sub>, CH<sub>3</sub>, and F<sup>5</sup>). The factor 1 in the

definition of  $P'$  shifts the scale to zero for hydrogen (X = H). The parameter  $P'$  gives a measure of the effective polarizing ability ( $\alpha$  or  $\gamma$ ) with respect to H, of the considered functional group X. The variation of  $P'$ , for a given substituent, indicates the effect of the substrate Y.

The functional groups with  $P' > 0$  are characterized by a polarizing ability, while those with  $P' < 0$  by a depolarizing capacity with respect to hydrogen.

Considering the relative property values, reported in Tables VI and VIII, of NH<sub>2</sub>OC, NHCH<sub>3</sub>OC, and N(CH<sub>3</sub>)<sub>2</sub>OC we observe that *N*-methylation leads to changes in  $\bar{\alpha}'$  which are approximately equal, while the variations in  $\bar{\gamma}'$  are quite different.

Studies of the groups HCH<sub>3</sub>N,<sup>2</sup> (CH<sub>3</sub>)<sub>2</sub>N, NH<sub>2</sub>OC, NHCH<sub>3</sub>OC, and N(CH<sub>3</sub>)<sub>2</sub>OC (Tables VI and VII) allow a comparison to be made on the effect of substituting H by CH<sub>3</sub> in different intramolecular environments. From the results of Table VIII we observe that the effect of methylation on the relative polarizability is larger in the amide groups than the amines. However, considering the relative hyperpolarizability, methylation of NH<sub>2</sub> (leading to HCH<sub>3</sub>N) has a larger effect than methylation of NH<sub>2</sub>OC (leading to NHCH<sub>3</sub>OC) while further substitution of HCH<sub>3</sub>N has a smaller effect than methylation of NHCH<sub>3</sub>OC. It is also seen that different orderings result for  $\alpha'$  and  $\gamma'$ . [The groups NHCH<sub>3</sub> and N(CH<sub>3</sub>)<sub>2</sub> have different positions in the scales of  $\alpha'$  and  $\gamma'$ .]

### IV. CONCLUSIONS

The amides have been chosen as model systems to analyze the effect of methylation, isomerism, and bonding and nonbonding interactions on  $\alpha$  and  $\gamma$ . The reported findings constitute part of a comprehensive and systematic study of the above effects employing  $\alpha$  and  $\gamma$  as probes.

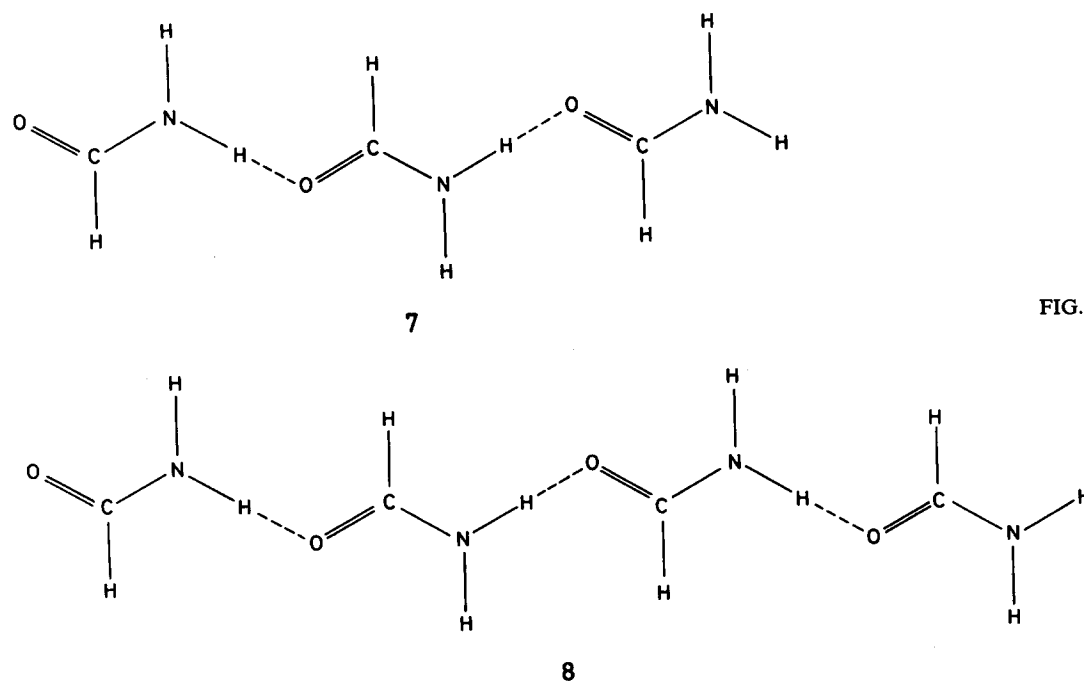


FIG. 3. Structure of (FA)<sub>2</sub> and (FA)<sub>4</sub>.

TABLE VI. Relative polarizabilities and hyperpolarizabilities of compounds containing the functional groups NH<sub>2</sub>OC, NHCH<sub>3</sub>OC, and N(CH<sub>3</sub>)<sub>2</sub>OC.

No. Molecule <sup>a,b</sup>	$\alpha'$	$\gamma'$	No. Molecule <sup>a,b</sup>	$\alpha'$	$\gamma'$	No. Molecule <sup>a,b</sup>	$\alpha'$	$\gamma'$
1 NH <sub>2</sub> COH	0.97	2.86	6 CH <sub>3</sub> NHCOH	2.37	3.86	14 (CH <sub>3</sub> ) <sub>2</sub> NCOH	4.06	6.71
2 NH <sub>2</sub> COCH <sub>3</sub>	1.24	3.59	7 CH <sub>3</sub> NHCOCH <sub>3</sub>	2.35	4.0	15 (CH <sub>3</sub> ) <sub>2</sub> NCOCH <sub>3</sub>	3.37	6.70
3 C <sub>2</sub> H <sub>5</sub> CONH <sub>2</sub>	0.82	1.81	8 C <sub>2</sub> H <sub>5</sub> CONHCH <sub>3</sub>	1.64	2.66	16 C <sub>2</sub> H <sub>5</sub> CON(CH <sub>3</sub> ) <sub>2</sub> <sup>c</sup>	2.31	3.87
4 C <sub>6</sub> H <sub>5</sub> CONH <sub>2</sub>	0.36	0.52	9 C <sub>6</sub> H <sub>5</sub> CONHCH <sub>3</sub>	0.84	0.82	17 C <sub>6</sub> H <sub>5</sub> CON(CH <sub>3</sub> ) <sub>2</sub> <sup>d</sup>	1.14	1.14
5 NH <sub>2</sub> CON(CH <sub>3</sub> ) <sub>2</sub>	0.56	0.78	10 NHCH <sub>3</sub> CONH <sub>2</sub>	2.10	1.31	18 (CH <sub>3</sub> ) <sub>2</sub> NCON(CH <sub>3</sub> ) <sub>2</sub>	1.58	1.77
			11 NHCH <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub>	0.99	1.44	19 (CH <sub>3</sub> ) <sub>2</sub> NCONHCH <sub>3</sub>	2.34	3.30
			12 (CH <sub>3</sub> NH) <sub>2</sub> CO <sup>e</sup>	1.39	1.81	20 (CH <sub>3</sub> ) <sub>2</sub> NCONH <sub>2</sub>	3.41	2.09
			13 (CH <sub>3</sub> NH) <sub>2</sub> CO <sup>f</sup>	1.68	1.74			

<sup>a</sup> For the molecular geometries data have been collected from the following sources: 1 : Ref. 29, 2 : Ref. 30, 3 : Ref. 30, 4 : Ref. 36, 5 : Ref. 37, 6 : Ref. 30, 7 : Ref. 30, 8 : Ref. 30, 9 : Ref. 30, 36, 10 : Ref. 37, 11 : Ref. 37, 12 : Ref. 37, 13 : Ref. 37, 14 : Ref. 31, 15 : Ref. 31, 16 : Ref. 30, 31, 17 : Ref. 36, 31, 18 : Ref. 37, 19 : Ref. 37, 20 : Ref. 37. The coordinates of all the molecules are available on request.

<sup>b</sup> Computation of the properties has been performed by employing. (i) The amide and amine group orbitals which have been defined (Sec. II). (ii) The ring C<sub>6</sub>H<sub>5</sub><sup>-</sup> orbitals are given in Ref. 16. (iii) The alkane (CH<sub>3</sub><sup>-</sup>, C<sub>2</sub>H<sub>5</sub><sup>-</sup>) orbitals are given in Ref. 13.

<sup>c</sup> Fully staggered.

<sup>d</sup> The methyl group is staggered with respect to the ortho H.

<sup>e</sup> The position of the second methyl group is similar to that of the monosubstituted urea Ref. 4.

<sup>f</sup> The methyl groups replace the two hydrogens which are furthest apart.

TABLE VII. Relative polarizabilities and hyperpolarizabilities of compounds containing the functional groups CH<sub>3</sub>HN and (CH<sub>3</sub>)<sub>2</sub>N.

No. Molecule <sup>a,b</sup>	$\alpha'$	$\gamma'$	No. Molecule <sup>a,b</sup>	$\alpha'$	$\gamma'$
1 NHCH <sub>2</sub> C <sub>2</sub> H	1.81	0.35	13 (CH <sub>3</sub> ) <sub>2</sub> NC <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	1.21	1.0
2 NHCH <sub>2</sub> C <sub>2</sub> NHCH <sub>3</sub> <sup>c</sup>	0.54	0.95	14 (CH <sub>3</sub> ) <sub>2</sub> NC <sub>2</sub> H	2.02	0.41
3 NHCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	1.27	2.31	15 (CH <sub>3</sub> ) <sub>2</sub> NH	2.26	1.33
4 NHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>3</sub> <sup>c</sup>	0.49	0.62	16 (CH <sub>3</sub> ) <sub>2</sub> NCH <sub>3</sub>	2.74	6.66
5 NHCH <sub>2</sub> CHCH <sub>2</sub>	1.33	1.81	17 C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	0.93	0.92
6 NHCH <sub>2</sub> CHCHNHCH <sub>3</sub> <sup>c</sup>	0.49	0.75	18 (CH <sub>3</sub> ) <sub>2</sub> NCONHCH <sub>3</sub>	1.17	1.46
7 NHCH <sub>2</sub> CONH <sub>2</sub>	1.04	0.69	19 (CH <sub>3</sub> ) <sub>2</sub> NCON(CH <sub>3</sub> ) <sub>2</sub>	0.87	0.76
8 NHCH <sub>2</sub> CON(CH <sub>3</sub> ) <sub>2</sub>	0.44	0.55	20 (CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>3</sub>	1.59	2.56
9 C <sub>6</sub> H <sub>5</sub> NHCH <sub>3</sub>	1.03	0.99	21 (CH <sub>3</sub> ) <sub>2</sub> NCHCHN(CH <sub>3</sub> ) <sub>2</sub> <sup>c</sup>	0.70	0.85
10 NH <sub>2</sub> CH <sub>3</sub>	0.94	0.32	22 (CH <sub>3</sub> ) <sub>2</sub> NCHCH <sub>2</sub>	1.98	2.0
11 (NHCH <sub>3</sub> ) <sub>2</sub> CO <sup>d</sup>	0.55	0.61	23 (CH <sub>3</sub> ) <sub>2</sub> NCONH <sub>2</sub>	1.90	1.26
12 (NHCH <sub>3</sub> ) <sub>2</sub> CO <sup>e</sup>	0.74	0.60			

<sup>a</sup> For the molecular geometries data have been collected from the following sources: 1 : Ref. 38, 39, 2 : Ref. 38, 39, 3 : Ref. 39, 40, 4 : Ref. 39, 40, 5 : Ref. 38, 39, 6 : Ref. 38, 39, 7 : Ref. 37, 8 : Ref. 37, 9 : Ref. 39, 41, 10 : Ref. 39, 11 : Ref. 37, 12 : Ref. 37, 13 : Ref. 38, 39, 14 : Ref. 38, 39, 15 : Ref. 39, 16 : Ref. 39, 17 : Ref. 39, 41, 18 : Ref. 37, 19 : Ref. 37, 20 : Ref. 39, 40, 21 : Ref. 38, 39, 22 : Ref. 38, 39, 23 : Ref. 37. Partial MNDO (QCPE 353) optimizer has been performed on the amine group and its bonding to the residue for 1, 2, 3, 4, 5, 6, and 9.

<sup>b</sup> The computation of the properties has been performed by employing the atomic orbitals defined in footnote b of Table VI.

<sup>c</sup> *Trans* configuration.

<sup>d</sup> *Cis* configuration.

TABLE VIII. The average relative properties of some functional groups.

No.	Functional group	$\bar{\alpha}' \pm \epsilon^a \times 10^2$	$\bar{\gamma}' \pm \epsilon^a \times 10^2$
1	F	- 7 ± 7	- 50 ± 24
2	H	0	0
3	NH <sub>2</sub>	38 ± 9	44 ± 50
4	CH <sub>3</sub>	60 ± 9	56 ± 39
5	NH <sub>2</sub> OC	79 ± 26	191 ± 105
6	HCH <sub>3</sub> N	89 ± 35	88 ± 42
7	(CH <sub>3</sub> ) <sub>2</sub> N	158 ± 55	175 ± 109
8	NHCH <sub>3</sub> OC	167 ± 45	220 ± 97
9	N(CH <sub>3</sub> ) <sub>2</sub> OC	260 ± 87	365 ± 253

<sup>a</sup>  $\bar{P}'$  is the average  $P'$  ( $\alpha'$  or  $\gamma'$ ) for the considered molecules, XY, and  $\epsilon$  is the variation of  $\bar{P}'$ . This variation is given by

$$\sum_i^n |(\bar{P}' - P'_i)|/n$$

and measures the effect of Y on the property values of X. This formula was misquoted in Ref. 5.

The cooperative character of the intermolecular interactions, employing some aggregates of formamide as test models, has been shown and the dependence of the properties on the shape of the aggregate has been discussed. The reported analysis is supplementary to the considerable amount of work performed on oligomers and multimers of amides.<sup>27</sup>

The main functional groups have been quantitatively analyzed employing various intramolecular environments. The following orderings of polarization have been established (we also report, for completeness, the relative properties of some other important functional groups<sup>5</sup>):

$$\alpha': \text{F} < \text{H} < \text{NH}_2 < \text{CH}_3 < \text{NH}_2\text{OC} < \text{HCH}_3\text{N}$$

$$< (\text{CH}_3)_2\text{N} < \text{NHCH}_3\text{OC} < \text{N}(\text{CH}_3)_2\text{OC},$$

$$\gamma': \text{F} < \text{H} < \text{NH}_2 < \text{CH}_3 < \text{HCH}_3\text{N} < (\text{CH}_3)_2\text{N}$$

$$< \text{NH}_2\text{OC} < \text{NHCH}_3\text{OC} < \text{N}(\text{CH}_3)_2\text{OC}.$$

To the best of our knowledge this is the first systematic attempt<sup>5</sup> to assess quantitatively the polarizing abilities of functional groups employing *both* the polarizabilities and second hyperpolarizabilities.

This study was performed using our CHF-PT-EB-CNDO method the reliability of which has been tested for monomers and was verified in the present work by producing reasonably accurate polarizability values for the considered amides. However, due to lack of experimental data, it is hard to define the errors of the reported aggregate property values. Thus, in order to ensure the validity of the findings, normalized results have been reported.

Finally, Hol *et al.*<sup>28</sup> suggested that the electric field generated by the backbone of a protein is a significant factor which must be included in the discussion of them. Thus it is expected that the study of appropriate model systems (like the ones considered here) will provide information and insight into the action of important biochemical systems.

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$$\alpha = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}),$$

$$\gamma = \frac{1}{3} (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz}),$$

where  $x$ ,  $y$ , and  $z$  denote Cartesian components. Expressions for the relevant tensor components, in terms of which  $\alpha$  and  $\gamma$  are defined, are given by McWeeny *et al.* (Ref. 19); (b) A. D. Buckingham and B. J. Orr, *Q. Rev. (London)* **21**, 195 (1967).

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