that serine serves diverse functions as (1) helix breaker, (2) participant in β turns and in β regions, (3) occasional helical residue, and (4) active-site residue. These diverse functions probably arise from the following characteristics of the -CH_2-OH side group: (1) small size (even the α-helical conformation being sterically allowed), (2) polar but nonionic structure, (3) capability of forming one or multiple hydrogen bonds, and (4) closeness to backbone which allows hydroxyl–peptide bond interactions.

(IV) Conclusion

Water-soluble copolymers of L-serine and N^5-(4-hydroxybutyl)-L-glutamine were synthesized and characterized. The *O*-trimethylsilyl group was found to be a suitable blocking group (with preservation of stereochemical configuration) for copolymerizations involving seryl residues. The thermally induced helix–coil transitions in water were examined over the temperature range of 0–80°, and the Zimm–Bragg parameters σ and s were determined by application of the host–guest technique[3–6] and the Allegra theory. The value of 0.78 found for s at 20° is a quantitative measure of the helix-breaking character of serine in water, and shows that serine is a less effective helix destabilizer than glycine. The computed values of s were insensitive to the value selected for the nucleation parameter σ below 7.5×10^{-5}. Assuming that σ, ΔH, and ΔS are independent of temperature in the range of 0–80°, the values of $\Delta G_{20°}$, ΔH, and ΔS were found to be 158 cal/mol, -101 cal/mol, and -0.9 eu, respectively. The various roles of serine in proteins are attributed to the small size, polar but nonionic structure, and ability to form one or more hydrogen bonds.

Acknowledgments. We wish to express particular appreciation to Dr. Ralph Hirschmann of Merck Sharpe and Dohme Research Laboratories, Division of Merck and Co., Rahway, N. J., who supplied the stereochemically pure *O*-trimethylsilyl-L-serine NCA, and to Dr. James Manning of The Rockefeller University, who determined the extent of racemization in the copolymers. Thanks are also due to Dr. Gerald Taylor both for helpful discussions and for additional experimental work in connection with the racemization problem, to Mr. Hua Tjan for the nitrogen and amino acid analyses, to Dr. V. S. Ananthanarayanan, Mrs. Patricia Von Dreele, Mrs. Karen Platzer, and Mr. Peter Lewis for many helpful discussions and assistance with the computer programs, and to Mrs. Jane Derbenwick for excellent technical assistance.

Conformational Properties of Structurally Rigid Polyamides. Conformation of Model Diamides

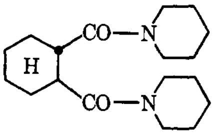
G. Montaudo,* P. Finocchiaro, P. Maravigna, and C. G. Overberger

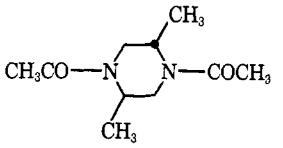
Institute of Industrial Chemistry, University of Catania, Catania, Italy, and Department of Chemistry and the Macromolecular Research Center, University of Michigan, Ann Arbor, Michigan 48104. *Received September 28, 1971*

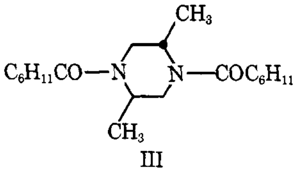
ABSTRACT: The conformational equilibria of some model diamides which represent the building blocks of a series of polyamides derived from *trans*-1,2-cyclohexanedicarboxylic acid and different aliphatic amines have been studied. We have used nmr and dipole moment measurements, coupled with some *a priori* conformational energy estimates, to ascertain the conformational preferences of diamides I, II, and III, which seem appropriate model compounds of polyamide IV (see text). The results indicate that diamide I exists preferentially in an extended conformation and that in diamides II and III the conformational equilibrium is strongly biased toward conformations containing axial methyl groups (nearly equipopulated mixture of the four diaxial rotamers possible). Nmr solvent differential shifts are also reported for some diamides, and the results are interpreted in terms of the collision complex concept.

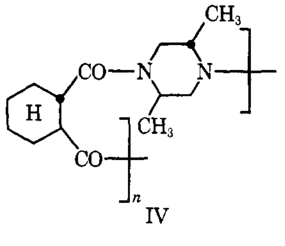
The optical properties of a series of asymmetric polyamides derived from cyclic 1,2- and 1,3-dicarboxylic acids, with varying degrees of rigidity imposed on the polymer chain, have been reported.[1] The results indicate that several of these polyamides may exist in preferred conformations in solution but cast no light on the identity of the specific conformations which may be present.[1]

To further investigate this problem, we have studied the conformational equilibria of some model diamides which represent the building blocks of our polymers. In the present approach we have used nmr and dipole moment measurements, coupled with some *a priori* conformational energy estimates, to ascertain the conformational preferences of diamides I, II, and III, which seem appropriate model compounds for polyamide IV.


I


II


III


IV

---

* Address correspondence to this author at the University of Catania.

[1] (a) C. G. Overberger, G. Montaudo, Y. Nishimura, J. Sebenda, and R. A. Veneski, *J. Polym. Sci., Part B*, 7, 219 (1969); (b) C. G. Overberger, G. Montaudo, M. Mizutori, J. Sebenda, and R. A. Veneski, *ibid., Part B*, 7, 225 (1969); (c) C. G. Overberger, R. A. Veneski, and G. Montaudo, *ibid., Part B*, 7, 877 (1969); (d) C. G. Overberger, G. Montaudo, Y. Nishimura, J. Sebenda, and R. A. Veneski, presented at the IUPAC Symposium, Budapest, 1969; (e) C. G. Overberger and Y. Shimokawa, *J. Polym. Sci., Part B*, 9, 165 (1971).

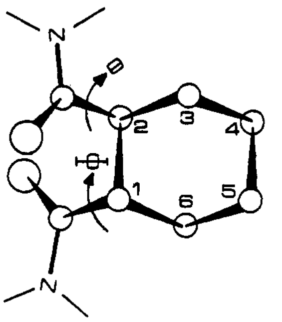
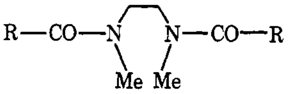


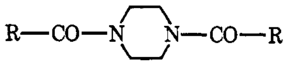
Figure 1. Internal rotation angles (ϕ and θ) for diamide I. The piperidine rings are omitted for clarity and only the cyclohexane ring is shown.

As reported in the companion paper,[2] the results obtained in the present investigation have been used in the study of the conformational properties of polyamide IV.

During our work, we have investigated a series of diamides (compounds V–X) derived from *N,N′*-dimethylethylenediamine (DMDE) and piperazine (PIP), which are the structural units of some polyamides used in the previous optical properties studies.[1]



V, R = CH_3
VI, R = C_6H_{11}
VII, R = C_6H_5



VIII, R = CH_3
IX, R = C_6H_{11}
X, R = C_6H_5

The conformational preferences of these diamides have already been studied by nmr,[3] and our data for these compounds do, in general, agree with those of previous workers.[3] We differ, however, in the interpretation of the nmr solvent effects, which proved of value in the nmr and conformational assignments, and only this point has been discussed.

Diamide from *trans*-1,2-Cyclohexanedicarboxylic Acid and Piperidine (I). Previous nmr and dipole moment data indicate that the substituents in the cyclohexane ring assume preferentially the diequatorial position in the case of *trans*-1,2-cyclohexanedicarboxylic acid and its alkyl esters.[4] We have now found that for diamide I nmr data indicate that the conformational equilibrium is strongly biased toward the diequatorial form. In fact, the cyclohexane tertiary protons resonate at 3.06 ppm ($CDCl_3$) and are seen as a quartet, as would be expected for the diequatorial form[4] (X part of an ABX system). Furthermore, inspection of molecular models reveals that the diaxial form is energetically disfavored and experiences sensible H–H and H–O van der Waals repulsion over the entire range of internal rotation angles.

As far as the conformational preference of diamide I is concerned, if the cyclohexane ring is taken as fixed with the substituents in the diequatorial position, and also considering the planar nature of the amide bonds, only two internal rotation angles (ϕ and θ, Figure 1) are needed in order to generate all the possible conformations.

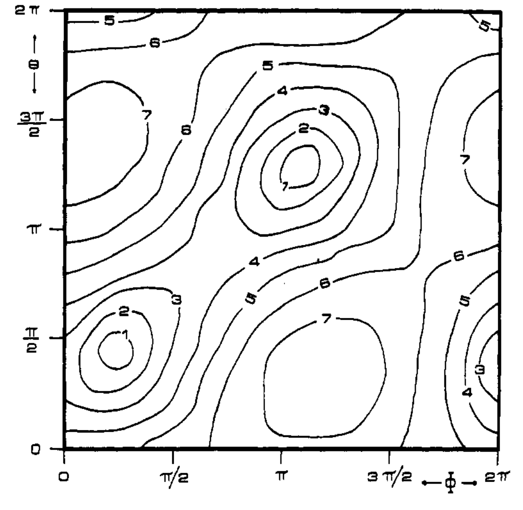
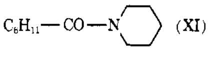
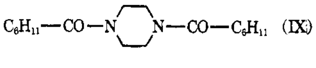
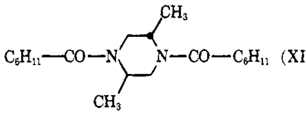
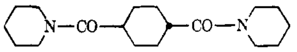


Figure 2. Contour map of calculated dipole moment (debyes) of diamide I as a function of the two internal rotation angles ϕ and θ. The conformation where the two C–O bonds are both eclipsed with respect to the C_1–C_2 bond was taken as $\phi = \theta = 0°$; ϕ and θ were rotated clockwise.

TABLE I
DIPOLE MOMENT DATA[a] IN BENZENE AT 25° OF SOME MODEL AMIDES

Compounds	a_ϵ	a_n	μ, D
 (XI)	8.22	0.032	3.84 ± 0.04
 (IX)	3.44	0.100	3.07 ± 0.04
 (XII)	3.31	0.109	3.14 ± 0.02
I[b]	1.56	0.102	2.03 ± 0.06
 (XIII)	2.56	0.138	2.61 ± 0.02

[a] $a_\epsilon = [(\epsilon_{12} - \epsilon_1)/W_2]_{W_2 \to 0}$, $a_n = [(n_{12}^2 - n_1^2)/W_2]_{W_2 \to 0}$; ϵ_1 is the dielectric constant of solvent, ϵ_{12} is the dielectric constant of the solution, W_2 is the weight fraction of solute, n_1 is the refractive index of the solvent, and n_{12} is the refractive index of the solution. [b] Racemic sample.

From inspection of Figure 1, it can be seen that the overall dipole moment of diamide I is subject to vary as the molecular conformation, since a variation of the internal rotation angles ϕ and θ causes a change in the relative orientation of the two highly polar amide groups.

A contour map of calculated[5] dipole moments as a function of ϕ and θ is shown in Figure 2. The experimental dipole

---

(2) See G. Montaudo, P. Maravigna, P. Finocchiaro, and C. G. Overberger, *Macromolecules*, **5**, 203 (1972).

(3) Y. Miron, B. R. McGarvey, and H. Morawetz, *ibid.*, **2**, 154 (1969).

(4) G. Montaudo and C. G. Overberger, *J. Amer. Chem. Soc.*, **91**, 753 (1969); C. G. Overberger, G. Montaudo, T. Furuyama, and M. Goodman, *J. Polym. Sci., Part C*, No. 31, 33 (1970).

(5) Dipole moments were calculated for each pair of ϕ and θ values by adding vectorially the bond moments resolved into their x, y, and z components. The individual moment contributed by each amide group was taken as 3.84 D (Table I), and its direction was assumed to form an angle of 39.6° with the C–N bond.[6] Interatomic distances and bond angles were deduced from pertinent literature data.[7] The map was generated starting from the conformation where the two C–O bonds are both eclipsed with respect to the C_1–C_2 bond ($\phi = \theta = 0°$) and rotating ϕ and θ clockwise.

(6) Y. Wada in "Poly-α-Amino Acids," G. D. Fasman, Ed., Marcel Dekker, New York, N. Y., 1967.

(7) E. Benedetti, P. Corradini, C. Pedone, and B. Post, *J. Amer. Chem. Soc.*, **91**, 4072 (1969); C. Pedone, E. Benedetti, A. Immizzi and G. Allegra, *ibid.*, **92**, 3549 (1970).

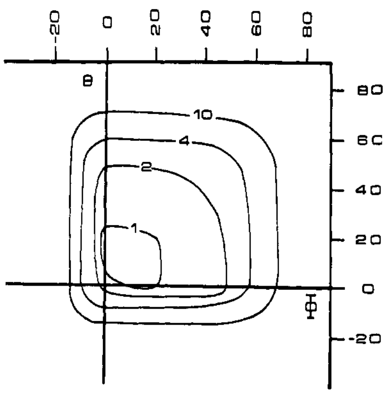


Figure 3. Contour map of the relative conformational energy of diamide I as a function of the two internal rotation angles ϕ and θ. Only contour lines of 10 kcal/mol or less are shown.

moment value (2.03 D; Table I) can be fitted only in two well-defined regions of the map. Of these, one ($\phi \simeq \theta \simeq 220°$) corresponds to a forbidden molecular conformation (the two piperidine rings should penetrate each other) and the other ($\phi \simeq \theta \simeq 40°$) corresponds to a molecular conformation where the two C–O bonds are both almost eclipsed with respect to the C_1–C_2 bond.

On the other hand, conformational energy estimates (Figure 3) show that the latter conformation comes very close to that of minimum energy. (The calculations were performed using pertinent literature data on interatomic distances and bond angles[7] and include nonbonded interactions. Coefficients for the pairwise Lennard-Jones potential functions were taken from Scott and Scheraga.[8a] Angular deformations, torsional potentials, and electrostatic interactions were also evaluated,[8b,c] but they were found to contribute to a minor extent to the conformational energy value (at least for the relevant map portion in Figure 3), so that the conformational energy map is sufficiently approximated to be compared with the experimental results.

Only the portion of the map around the minimum has been traced in Figure 3, since steric overlaps cause the conformational energy to exceed its minimum value prohibitively over the remaining range of ϕ and θ values.

The agreement between *a priori* conformational energy estimates and dipole moment data appears good enough, and the overall evidence indicates the nearly "eclipsed" (extended)[9] form as the preferred conformation in diamide I.

Diamides from *trans*-2,5-Dimethylpiperazine. Two diamides of this type (compounds II and III) have been studied. No appreciable differences are found in the nmr spectra of these two compounds (apart from the cyclohexane absorption), so only the diacetyl derivative II will be discussed here.

If the piperazine ring is assumed in the usual chair form,[10] the two ring methyls in amide II can assume either the diaxial or the diequatorial position. Owing to the presence of two asymmetric carbon atoms and to the kinetically restricted rotation around the amide bonds, four rotamers are expected to contribute to the nmr spectrum of the diaxial and diequatorial forms, respectively (Figure 4). (Forms A_1 and A_2 (E_1 and E_2 as well) are enantiomers (*i.e.*, identical by nmr). Forms A_3 and A_4 (E_3 and E_4 as well) have inversion centers (corresponding groups *in each* identical).)

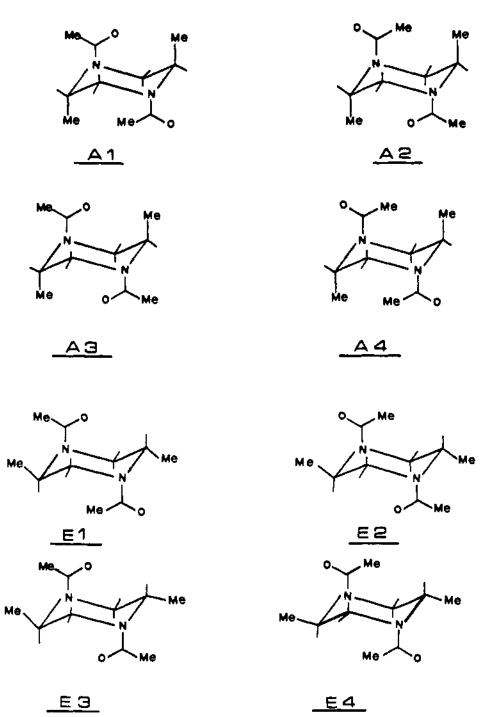


Figure 4. Possible rotamers of *N*,*N*′-diacetyl-*trans*-2,5-dimethylpiperazine.

Our nmr data provide evidence that in diamide II the conformational equilibrium is strongly biased toward conformations containing axial methyl groups (nearly equipopulated mixture of the four diaxial rotamers possible).

The 100-MHz spectrum ($CDCl_3$) of II is reported in Figure 5. Four methyl doublets appear crowded in the region between 1.10 and 1.30 ppm. (Only six lines are actually seen in the spectrum of Figure 5. The four doublets were, however, clearly detected by decoupling experiments (Table II). At higher temperature (110°) the four doublets coalesced to yield one doublet.)

This spectral feature, while clearly showing that the compound exists at room temperature as a nearly equipopulated mixture of four rotamers, rules out the possibility that all these four rotamers carry equatorial methyls. In fact, if this were the case, some methyls would experience the deshielding effect of the carbonyl and others would not (forms E1–E4, Figure 4), so that two well-separated groups of methyls should be seen in the spectrum.

Moreover, the only way to combine the evidence for the existence of four rotamers with the observed relative intensities of the signals [4.90 (1), 4.37 (0.5), 4.24 (0.5), 4.03 (1), 3.45 (2), 3.05 (0.5), 2.95 (0.5), 2.20 (6), 1.20 (6)] is to choose the four diaxial forms (A1–A4, Figure 4), and a detailed analysis of the spectral fine structure (reported in Table II) confirms this choice. Notably, the equatorial protons in an eclipsed position to the carbonyl experience a strong deshielding effect (about 0.9 ppm, Table II) with respect to the unexposed equatorial protons. As expected, for the axial protons the deshielding is nearly halved (about 0.45 ppm, Table II).

---

[8] (a) R. A. Scott and H. A. Scherega, *J. Chem. Phys.* 45, 2091 (1966); 46, 4410 (1967); R. F. McGuire, G. Vanderkooi, F. A. Momany, R. T. Ingwall, G. M. Crippen, N. Lotan, R. W. Tuttle, K. L. Kashuba, and H. A. Scheraga, *Macromolecules*, 4, 112 (1971); (b) D. Del Re, *J. Chem. Soc.*, 4031 (1958); (c) D. Poland and H. A. Scheraga, *Biochemistry*, 6, 3791 (1967).

[9] Although the term *extended conformation* better indicates a conformation in which both the carbonyls are in diaxial positions, we have used this term here (and in the companion paper) to describe *the most extended conformation among those with diequatorial carbonyls.*

[10] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison in "Conformational Analysis," Interscience, New York, N. Y., 1966, p 250.

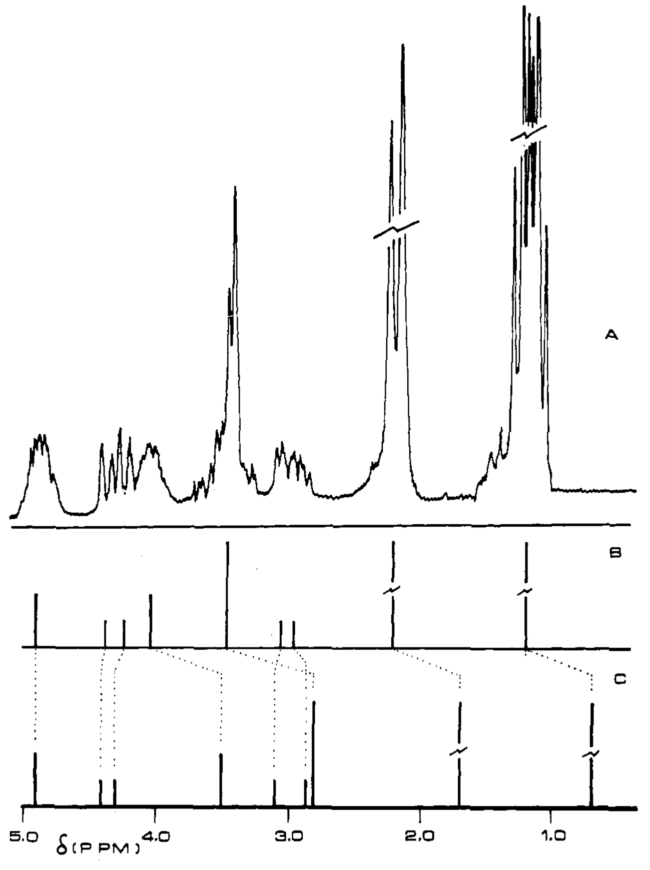


Figure 5. Nmr spectra (100 MHz) of *N*,*N'*-diacetyl-*trans*-2,5-dimethylpiperazine at 30°: (A) spectrum in $CDCl_3$, (B) schematic spectrum in $CDCl_3$, (C) schematic spectrum in benzene.

These figures compare well with those reported for pertinent protons in some alkylpiperidine amides.[11]

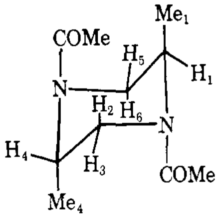
The observed chloroform/benzene differential shifts, schematically reported in Figure 5, are in agreement with those expected for a nearly equipopulated mixture of the four diaxial rotamers (A1–A4, Figure 4). In fact, assuming that the geometry of the solute–solvent collision complex is similar here to that found for the PIP and DMDE diamides (see next section), only four signals are expected, and found, to be unshifted in the benzene spectrum (Figure 5).

Conformational energy estimates and dipole moment data confirm the nmr results. Molecular model work shows that methyl–methyl contacts for rotamers E1, E2, and E3 (Figure 4) are so unfavorable as to rule out these forms from the conformational equilibrium; only E4 can be considered further. On the contrary, owing to the axial position of the methyls, the four diaxial rotamers (Al–A4, Figure 4) appear, to a first approximation, equienergetic.

Only one H–H and one H–O distance need to be considered, in order to estimate the conformational energy difference among these axial rotamers and the E4 form. The nonbonded atom interaction computed in this way indicate an energy difference of about 10 kcal/mol in favor of the diaxial rotamers. (The calculations were performed using literature data on interatomic distances and bond angles[7] and include nonbonded interactions, angular deformations, and torsional potentials. Coefficients for the pairwise Lennard-Jones potential functions were taken from Scott and Scheraga.[8a])

TABLE II

NMR DATA ($CDCl_3$, 100 MHz), FOR 2,5-*trans*-DIMETHYL-*N*,*N'*-DIACETYLPIPERAZINE



Rotamer[a]	H_1	H_2	H_3	H_4	H_5	H_6	Me_1	Me_4	MeCO
A1	4.90[b]	3.45[c]	3.45[c]	4.03[b]	4.37[d]	2.95[e]	1.23[f]	1.26[g]	2.20[h]
A2	4.03[b]	2.95[e]	4.37[d]	4.90[b]	3.45[c]	3.45[c]	1.26[g]	1.23[f]	2.20[h]
A3	4.03[b]	3.05[e]	4.23[d]	4.03[b]	4.23[d]	3.05[e]	1.32[g]	1.32[g]	2.20[h]
A4	4.90[b]	3.45[c]	3.45[c]	4.90[b]	3.45[c]	3.45[c]	1.12[f]	1.12[f]	2.20[h]

[a] See Figure 4. [b] Methine complex multiplet. By irradiation at 3.45 ppm it is partially resolved in an AB_3 quartet ($J \simeq 7.0$ cps). By irradiation at 1.2–1.3 ppm it is partially resolved in a triplet ($J_{a,e} \simeq 3.5$ cps). [c] Methylene complex multiplet. [d] Equatorial doublet ($J_{gem} \sim 14.0$ cps, $J_{e,e} \sim 2.0$ cps). [e] Axial quartet ($J_{gem} \sim 14.0$ cps, $J_{a,e} \sim 4.0$ cps). [f] Methyl doublet ($J \sim 7.0$ cps). Coalesces by irradiation at 4.90 ppm. [g] Methyl doublet ($J \sim 7.0$ cps). Coalesces by irradiation at 4.03 ppm. [h] Chemical shift value from the coalesced signal of a high-temperature spectrum. Acetyl signals appear as a doublet in the room-temperature $CDCl_3$ spectrum (Figure 2). In phenol, however, the expected four signals are seen.

TABLE III

SOLVENT SHIFTS[a] OF *N*-METHYLENE PROTONS[b] OF STRUCTURALLY RELATED DIAMIDES

Compound	$\Delta_1 = \delta(CHCl_3) - \delta(C_6H_6)$, ppm	$\Delta_2{}^c = \delta(CHCl_3) - \delta(C_6H_5OH)$, ppm
V	+0.29	+0.40
VI	+0.23	+0.25
VII	+0.20	+0.38
VIII	+0.58	+0.46
IX	+0.48	+0.44
X	+0.46	+0.26

[a] Chemical shifts measured at 38° in parts per million downfield from TMS as internal standard (60 and 100 MHz). [b] Average value calculated from the experimental signals corresponding to the cis and trans forms. [c] 90% aqueous phenol.

Even allowing for angular deformation in order to minimize the van der Waals interaction, the energy difference remains too high, and rotamer E4 has to be considered disfavored. No attempt has been made to calculate rigorously eventual energy differences among the four diaxial rotamers.

The experimental dipole moment value for amide III (3.14 D, Table I) comes close to the calculated value (3.50 D) for the equipopulated mixture of the four diaxial rotamers.

Nmr Solvent Effects in Diamides from Dimethylethylenediamine and Piperazine. Unusually drastic nmr solvent effects have recently been observed,[3] for some of the diamides in Table III, going from chloroform to aqueous phenol solutions. Interaction between phenol and the amide molecule results in a significant increase in the chemical shift difference for signals corresponding to cis and trans amide isomers. This effect was attributed to hydrogen bonding of the phenol to the carbonyl oxygen of the amide. Hydrogen bonding, in this case, was

---

(11) (a) D. M. Lynch and W. Cole, *J. Org. Chem.*, 31, 3337 (1966); (b) R. A. Johnson, *ibid.*, 33, 3627 (1968).

believed to magnify the normal diamagnetic shielding of the aromatic nuclei.[3]

We have found, however, that benzene gives solvent shifts quite comparable to those of phenol (Table III), ruling out the hydrogen-bonding hypothesis. It is true that cis and trans amide peaks appear sometimes (compounds VII and X, Table III) more "resolved" in phenol, but this is merely the effect of a higher coalescence temperature of the cis and trans amide signals in this solvent. Amides with high enough coalescence temperatures[3,12] (compounds V, VII, and VIII; Table III) show practically identical spectra both in benzene and in phenol.

Collision complexes of amides with benzene are well known.[13] Straightforward application of the collision complex concept[13,14] has allowed us to account, at least qualitatively, for the solvent shifts found in the nmr spectra of the above diamides (Figure 6). Only structures directly detectable from the spectra have been reported in Figure 6. For compounds V, VI, and VII, the ratio cis/cis to trans/cis has been found to be very close to 50:50. The same ratio (cis to trans) is found for compound VIII.

Separate signals due to cis and trans forms are not detectable in the spectra of compounds IX and X. Dipole moment data (Table I), however, show that compound IX exists as a mixture 1 : 1 of cis and trans forms.

As recently pointed out,[14] the potential applications of the collision complex concept have been somewhat neglected, possibly because of the lack of a generally accepted model for solute–solvent collision complexes.[14] In the present case, besides helping to assign the nmr signals, the above concept has provided a molecular model which might be used as an independent source of conformational information.

Experimental Section

The commercially available reactants were further purified according to the literature.

trans-1,4-Cyclohexanedicarbonyl chloride was prepared from the corresponding acid with $SOCl_2$; mp 68° (lit.[15] mp 69°).

(±)-*trans*-1,2-Cyclohexanedicarbonyl chloride was obtained according to the literature,[4] from *cis*-1,2-cyclohexanedicarboxylic anhydride.

Analytical Procedures. Infrared spectra were recorded on a Perkin-Elmer 237 infrared spectrophotometer; nmr spectra were obtained on Varian A60 or HA-100 analytical spectrometers, equipped for variable-temperature work.

Molecular weight determinations were obtained by vapor pressure osmometry using a Mechrolab 301A thermoelectric osmometer, in dichloroethane at 50°.

Melting points (uncorrected) were obtained in glass capillary tubes sealed under vacuum and checked with a Kofler hot-stage microscope.

Elemental analyses were obtained commercially.

Dipole Moments. The dielectric constants were measured in benzene solution at 25 ± 0.02° with a DM 01 Dipolmeter WTW working at 2 MHz.

Benzene 99.9% (Merk) was dried over molecular sieves.

The dielectric constant of benzene was taken[16] to be 2.2725 at 25°. Attainable measuring sensitivity is of about two units in the fourth decimal place in the dielectric constant. For the refractive index measurements was used a differential refractometer, BP 2000 V Brice-Phoenix, which measured the difference in refractive index between a solution and benzene as solvent, at 25°. Since this apparatus is equipped with a mercury vapor lamp, Δn values measured at 436 and 546 mμ were reported at the sodium line values using the Chauchy dispersion formula, and the refractive indices of benzene were taken as 1.51979 at 436 mμ, 1.5021 at 546 mμ, and 1.49772 at 589 mμ[16] at 25°.

The differences between Δn values measured at 546 mμ and reported at 589 mμ were very small, sensible only at the fifth decimal place. Use of the above instrument, although time consuming, allows limiting measuring sensitivity of about three units in the sixth decimal place of the refractive index difference.

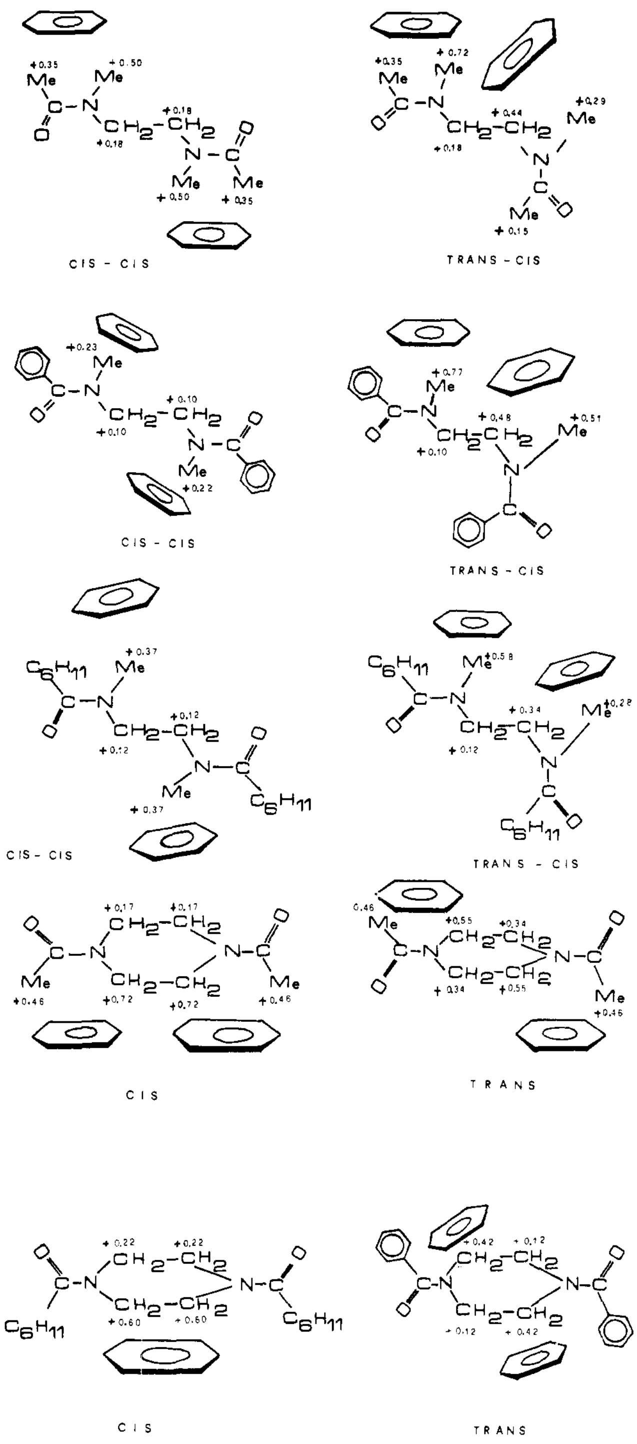


Figure 6. Geometry of collision complexes of diamides with aromatic solvents.

---

(12) M. T. Roger and J. C. Woodbray, *J. Phys. Chem.*, **66**, 540 (1962).

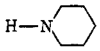
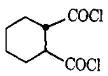
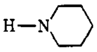
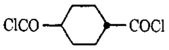
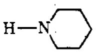
(13) H. V. Hatton and R. E. Richards, *Mol. Phys.*, 3, 253 (1960); 5, 139 (1962).

(14) T. Ledaal, *Tetrahedron Lett.*, 1683 (1968).

(15) R. Malachowski, J. J. Wasowska, S. Jozkiewicz, J. Adamiczka, and G. Zimmerman-Pasternak, *Ber. Deut. Chem. Ges. B*, **71**, 759 (1938).

(16) Landolt-Bornstein, Springer-Verlag, Berlin, 1967, Bd II/621, Bd II/8, 635.

TABLE IV
SYNTHESIS AND CHARACTERISTICS OF AMIDES

Compound	Starting materials (mol)		Yield, %	Solvent or n_D[a]	Mp or K_p, °C (mm)	Mol wt[d] Calcd	Mol wt[d] Found	Amide band, cm^{-1}	Nmr[b]
XI[c]	$C_6H_{11}COCl$ (0.021)	 (0.023)	75	n_D^{17} = 1.5075	102 (0.5)	195.3	210	1,650	1.68 (16 H, m), 2.52 (1 H, m), 3.62 (4 H, m)
VI	$C_6H_{11}COCl$ (0.11)	DMDE (0.05)	85	Ligroin	94–95	308.4	312	1,630	1.30 (6 H, s), 1.67 (20 H, m), 2.45 (2 H, m), 2.93, 3.06 (2 H, s), 3.46, 3.50 (2 H, s)
IX	$C_6H_{11}COCl$ (0.075)	PIP (0.035)	90	Ligroin	213–215	306.4	311	1,650	1.66 (20 H, m), 2.45 (2 H, m), 3.52 (8 H, s)
II	CH_3COCl (0.09)	DMP (0.04)	30	Benzene–ligroin	165–167	198.3	201	1,630	See Table IV
XII	$C_6H_{11}COCl$ (0.04)	DMP (0.016)	80	Benzene–ligroin	201–203	334.2	334	1,650	1.25 (6 H, d), 1.75 (20 H, m), 2.42 (2 H, m), 2.94 (0.5 H, q), 3.05 (0.5 H, q), 3.46 (2 H, m), 4.14 (1 H, m), 4.28 (0.5 H, d), 4.42 (0.5 H, d), 4.90 (1 H, m)
I	 (0.015)	 (0.034)	87	Ligroin	114–115	306.4	320	1,635	1.60 (20 H, m), 3.06 (2 H, X part of ABX system), 3.50 (8 H, m)
XIII	 (0.015)	 (0.034)	83	Ligroin	182–184	306.4	305	1,645	1.70 (20 H, m), 2.68 (2 H, m), 3.63 (8 H, m)

[a] Crystallization solvent or refractive index. [b] Chemical shifts measured in ppm downfield from TMS as internal standard ($CDCl_3$, 60 or 100 MHz at 30°C). [c] M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdoun, *Bull. Soc. Chim. Fr.*, 1042 (1952), report K_{p5} = 150°. [d] Measured by vpo in dichloroethane at 50°.

The dipole moments were calculated as described by Guggenheim.[17]

The final formula (benzene 25°) is

$$\mu^2\ (D^2) = (0.009208)M(a_\epsilon - a_n)$$

Probable error of our measurements is ±0.05 D.

Synthetic Procedures. The amides listed in Table IV were obtained by treating equimolecular amounts of the acid chloride with the amine dissolved in dry benzene at 20°, under stirring, in the presence of triethylamine. The hydrochloride of the triethylamine formed instantaneously, and after about 5 min the mixture was poured into water, neutralized, extracted with $CHCl_3$, and dried (Na_2SO_4); the solvent was removed under reduced pressure. The crude product obtained was washed with ether and crystallized. All the compounds in Table IV analyzed correctly. The amines already known in the literature (unreported in Table IV) were obtained in a similar way; the physical constants were found identical with those reported in literature.[3]

Acknowledgment. The authors are grateful for financial support by the U. S. Army Research Office (Durham), under Grant No. DAHCO4-69-C-0050, for a portion of this work, and by the LTPR Center (Italian CNR) at Arco Felice, Naples.

---

(17) E. A. Guggenheim, *Trans. Faraday Soc.*, 47, 573 (1951).