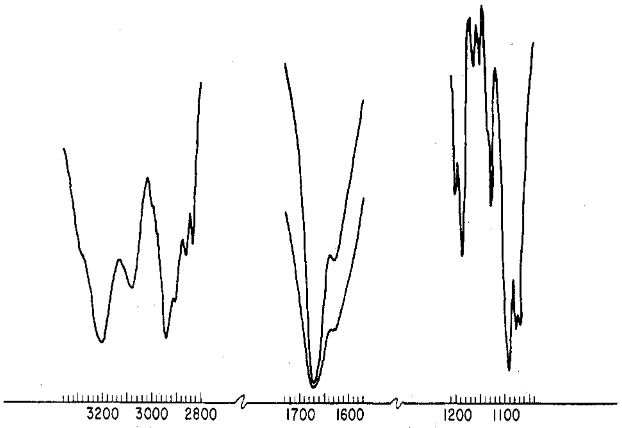


Figure 1.—Infrared spectrum of β-methoxy-ε-caprolactam.

appear to be well founded in light of results obtained in studies on caprolactam derivatives carried out in our laboratory. Although it had been shown that substituted caprolactams can be obtained from α-bromocaprolactam by nucleophilic substitution,[2,3] the reaction between the latter and a strong base such as sodium alkoxide was found to be governed by a quite different mechanism. Nevertheless, to verify the available information, α-bromocaprolactam and sodium methoxide were allowed to react according to both the procedure given in ref 1 and a modified one which gave the same reaction product but in a higher yield (60%). The modified procedure resembled one reported earlier[4] and differed from that given in ref 1 mainly by eliminating the vacuum distillation of the reaction product. Purification was achieved by crystallization from a chloroform–petroleum ether (bp 30–50°) system. An analytically pure sample, mp 62°, was obtained in either case by recrystallization from petroleum ether. A melting point of 54–55° was reported in ref 1. *Anal.* Calcd for $C_7H_{13}NO_2$: C, 58.68; H, 9.15; N, 9.78. Found: C, 58.68; H, 9.43; N, 9.89.

Considering the results of previous studies[4] on similar compounds, the reaction product was identified by spectroscopic analyses to be not the α-methoxy- but the β-methoxy-ε-caprolactam. The significant bands of the infrared spectrum (KBr, Beckman IR9) are shown in Figure 1. They are 3205, 3080 (NH stretching); 2860, 2830 (methoxy, CH stretching); 1670 (amide I); 1072, 1080, 1090 [C–O asymmetrical stretching, this triplet seems to be characteristic for the isopropyl ether moiety $>(CH_2)_2CHOCH_3$].

The 100-MHz nmr spectrum is shown in Figure 2; it consists of four major groups, the integral of which correspond to the proportional relation of 1:6:2:4.

The most significant signal is the triplet centered at about 2.75 ppm which has been attributed to the protons of the methylene group located between a carbonyl group and a carbon linked to an ether oxygen.[4]

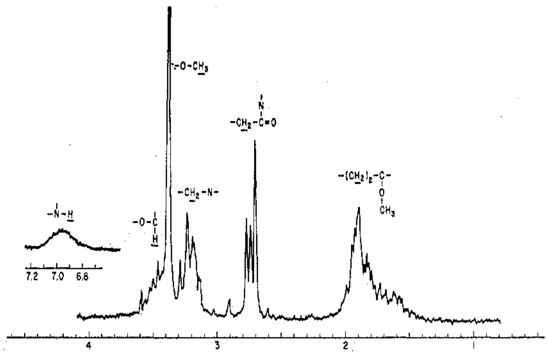
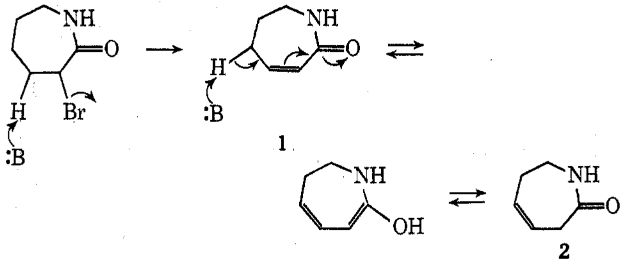


Figure 2.—Nmr spectrum of β-methoxy-ε-caprolactam.

The formation of the β derivative may be explained by a mechanism that entails elimination of HBr, followed by nucleophilic addition of the methoxide anion to the formed unsaturated lactam. It was shown earlier[4] that treating α-bromocaprolactam with a strong base can yield both 1,5,6,7- and 1,3,6,7-tetrahydro-2*H*-azepin-2-one (**1** and **2**, respectively). This can be rationalized by a mechanism such as shown below.



Isomerization of the β,γ-unsaturated lactam **2** into the α,β-unsaturated **1** can easily be visualized for the reaction conditions employed.

Typical 1,4 addition involving **1** yields then as the principal reaction product, the β-methoxy-ε-caprolactam.

There is no disagreement with the phenomenological aspects of the paper by Kondeliková, *et al.;* however, any conclusions regarding the behavior of the lactam as a function of the position of the methoxy group may need revision.

Registry No.—α-Bromo-ε-caprolactam, 3457-66-7; sodium methoxide, 124-41-4; β-methoxy-ε-caprolactam, 36982-61-3.

Acknowledgment.—The author wishes to thank Mrs. L. S. Komarowski for the infrared spectra and Messrs. G. E. Babbitt and R. L. Lapinski for the nmr spectra.

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Conformational Properties of 2,2′-Disubstituted Diphenyl Ethers and Sulfides by Dipole Moments. A Reexamination

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The conformational properties of diphenyl ethers (DPO) and diphenyl sulfides (DPS) in solution have received continued attention up to recently, and several workers have resorted to dipole moment (DM)

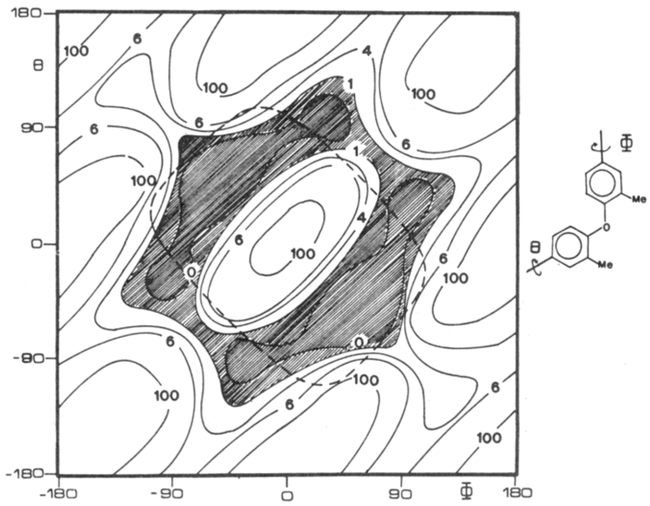


Figure 1.—Energy contour map (kcal/mol) of 2,2′-dimethyldiphenyl ether. Energy values are relative to the conformation of minimum energy. The shaded area corresponds to the energetically allowed region. The dotted superimposed line corresponds to the experimental (0.83 D) isomoment line.

measurements of 2,2′-disubstituted derivatives in an attempt to ascertain the conformational properties of these compounds.[1-6]

Dipole moments, being conformation dependent, are very useful in this kind of study, but sometimes do not provide unequivocal information since different conformations may be calculated to have the same DM value.

In spite of this difficulty, definite conformational assignments have been repeatedly reported for several 2,2′-disubstituted DPO and DPS, on the basis of DM data.[1,2,4,6]

During an nmr study[7a,b] of the conformational properties of ortho-substituted DPO and DPS, we have noted that no definite conformational preferences can be associated with the 2,2′ derivatives. Therefore, nmr and DM data seem to be in conflict and we have found it opportune to reexamine the problem on energetic grounds.

Results and Discussion

The contour maps of calculated DM as a function of the two internal rotation angles for compounds in Table I reveal that several different conformations have the same calculated DM value.[1,4,6] Furthermore, the experimental DM values (Table I) come surprisingly close to the values corresponding to a thermodynamically unrestricted rotation of the phenyl rings.

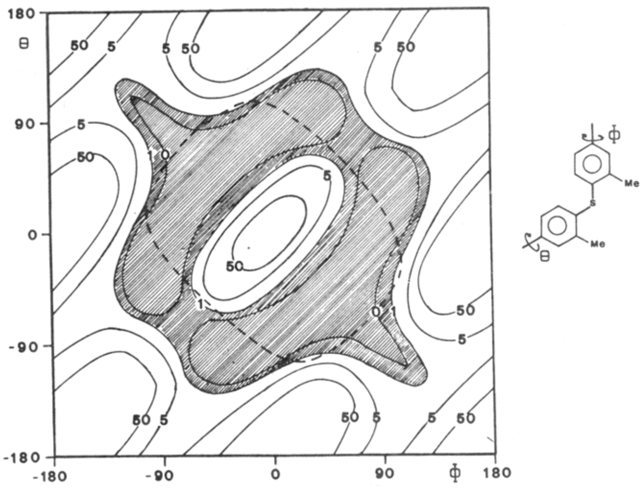
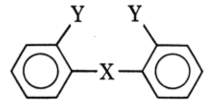


Figure 2.—Energy contour map (kcal/mol) of 2,2′-dimethyldiphenyl sulfide. Energy values are relative to the conformation of minimum energy. The shaded area corresponds to the energetically allowed region. The dotted superimposed line corresponds to the experimental (1.18 D) isomoment line.

TABLE I

EXPERIMENTAL AND CALCULATED DM VALUES FOR 2,2′ DERIVATIVES OF GENERAL FORMULA I



I

No.	X	Y	μ_{exptl}	$\mu^{a}_{free\ rotation}$
1	O	CH_3	0.83[b]	1.07
2	O	I	2.72[b]	2.40
3	O	NO_2	6.64[b]	5.80
4	S	CH_3	1.18[c]	1.40
5	S	Cl	3.33[c]	3.15
6	S	NO_2	6.89[d]	6.20

[a] Calculated for the free rotating molecules according to reference 1. [b] Reference 1. [c] Reference 4. [d] Reference 6.

Based exclusively on such data, it appears hazardous to speculate about possible conformational preferences of these compounds, as the previous authors have done.

On the other hand, the existence of a specific preferred conformation cannot be excluded *a priori*, if it happens to have a DM value coincident with the experimental one (Figures 1 and 2).

This ambiguity can be removed by complementing the DM with energetic considerations, and we have used semiempirical conformational energy calculations to build contour maps of relative conformational energy as a function of the two internal rotation angles for 2,2′-dimethyl DPO and DPS (Figures 1 and 2, respectively).

Inspection of the contour maps in Figures 1 and 2 reveals that large regions of the conformational space are "energetically allowed"[7c] shaded area in Figures 1 and 2), so that the molecular population becomes distributed over a wide range of torsional angles and the experimentally observed DM values can be properly interpreted as a weighted average of the DM contributions of separate species.

The experimental DM values of the chloro and nitro derivatives (Table I) are so close to those calculated for the free rotating molecules that their energy con-

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tour maps are likely to resemble those of the methyl derivatives, as should be expected by comparing only their relative van der Waals radii. Accordingly, also for these compounds the observed DM should be interpreted as a weighted average of the DM contributions from the overall range of allowed conformations.

The situation is similar in 2,2′,4,4′-tetranitrodiphenylmethane,[8] for which the experimental DM value (4.25 D) comes close to that calculated for the free rotating molecule (5.25 D).

Under these circumstances, it appears incorrect to associate the experimental DM values in Table I with a specific conformation,[1,4,6] and the situation seems to be best rationalized by considering these molecules as experiencing an almost complete thermodynamically unrestricted rotation.

On evaluating our results, it appears that the comparison of experimental and calculated DM is insufficient to reach unequivocal conclusions about the conformational properties of the title compounds and that a knowledge of the potential energy–internal rotation profiles is necessary to evaluate the DM data properly. More specifically, when the energy contour maps show a lack of conformational preference, immaterial of the technique employed, one should not try to interpret the experimental data in terms of specific preferred conformations.

Calculations

Calculations were performed with the help of a microcomputer, Hewlett-Packard Model 9100 B.

The starting conformation ($\Phi = \theta = 0°$) for the compounds studied was taken with both rings planar, and the origin of the axes was placed at the bridge atom. Interatomic distances and natural bond angles were taken from pertinent literature data.[9,10]

Distances among all the atoms were computed for each pair of Φ and θ values calculating first (trigonometrically) the atomic coordinates for each atom for a fixed conformation and then applying the usual rotation matrix method.[11]

The energy for nonbonded interactions was obtained from the calculated distances using the Lennard-Jones potential.[12]

Torsional energies were not taken into account because they were found to be negligible.[13] Individual energy values for each one of the interacting pairs considered were added together, obtaining the total strain energy (unminimized) for each pair of Φ and θ values from 0 to 360°, with a stepwise 10° increment.

The strain energies found were minimized according to a procedure described in a previous paper[14] and the necessary bending constants were taken from the literature.[15-17]

Dipole moments were calculated, for each pair of Φ and θ values, adding vectorially the x, y, and z components of the individual bond moments. The individual moments and bond angles used were the same as reported in the references.[1,4,6] The values of the dipole moment for the free rotating molecules were calculated according to the literature.[1]

Registry No.—2,2′-Dimethyldiphenyl ether, 4731-34-4; 2,2′-dimethyldiphenyl sulfide, 4537-05-7.

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