the information required to correctly classify the sample.

The results of Turner, Tinoco, and Maestre (eq 1 and 2 of ref 1) are identical with those exhibited for cases 3 and 4 of Table I except for a factor of ln 10/2 which seems to be missing in eq 2 of ref 1. We note that case 2 and 3 of Table I could be obtained from case 4 if the appropriate combination of limiting procedures is used.

The thrust of our program is the detection of backward scattered fluorescence light, an experimental configuration suitable for the scanning of opaque samples, possibly solid and possibly of nonuniform composition. Focused laser excitation is used for this purpose, and further results will be submitted for publication in the near future.

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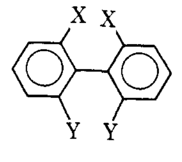
An Optical Rotatory Dispersion Study of the Conformation of Optically Active Biphenyls in Solution

Sir:

The preferred geometry of biphenyl varies considerably with experimental conditions. The torsional angle between the rings has been variously reported to be 42-45° (gas phase),[1] 0° (crystalline),[2] and 20° (solution).[3] When the torsional angle, ϕ, is neither 0 or 90°, biphenyl exists in two enantiomeric conformations, IIa and IIIa (with torsional angles ϕ and $180° - \phi$), that can interconvert by traversing a transition state at either 0 or 90° (see Figure 1).

Although substituted biphenyls of the type I have long been known to have torsional angles different from 0, 90, and 180° (0° is defined as X eclipsing X) in both the gas[4] and solution[5] phases, no evidence for the exisence of more than one conformation between $\phi = 0$ and 180° was presented. We present evidence in support of the existence of two equilibrating conformations ($0° < \phi < 180°$) for several optically active biphenyls. If two conformations ($0° < \phi < 180°$) exist for optically active biphenyls such as Ib-e, the relationship between energy and torsional angle be-



Ia, X = Y = H
b, X = CH_3; Y = NO_2
c, X = COOH; Y = NO_2
d, X = CH_2OH; Y = NO_2
e, X = CH_2Br; Y = NO_2

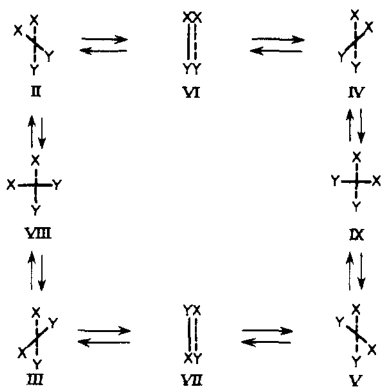


Figure 1. Possible conformations of substituted biphenyls.

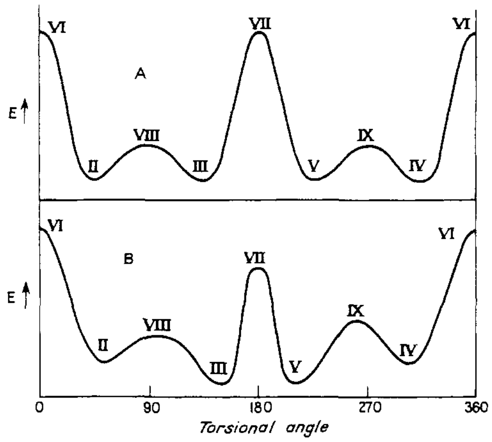


Figure 2. Energy vs. torsional angle for (A) biphenyl; (B) optically active biphenyls such as Ib or Ic. The values of the extrema are chosen for illustrative purposes only.

comes more complicated than that for biphenyl, itself (see Figure 2). The potential barriers at 0 and 180° no longer are of equal magnitude. The potential barriers that were at 90 and 270° are generally shifted somewhat from these angles. Notably, IIb-e and IIIb-e are no longer enantiomers but diastereomers. Thus, IIb-e and IIIb-e differ in energy. Assuming the barrier at 90° to be small, IIb-e and IIIb-e will be in equilibrium, with their relative populations determinable from a Boltzmann distribution.

If we consider the groups X and Y to be perturbations on Ia, we expect IIb-e and IIIb-e to have opposite chirality (and molecular rotation) since IIa and IIIa are enantiomers (this has been predicted[5a] from the theory of Kirkwood[6] for the transition near 260 nm). Thus, a small change in the relative populations of IIb-e should result in a significant change in the observed molecular rotations of Ib-e.

The ORD spectra of Ib-e have been measured as a function of temperature. The results for the λ_{max} nearest 260 nm (the transition due to the chirality of the phenyl-phenyl twist[5]) are collected in Table I. The spectra were measured in a thermostated cell using a Durrum-Jasco J-20 spectrometer. After the temperature was varied, the initial spectrum was remeasured. No racemization was detected for any of the compounds studied. The behavior of Ib in *n*-octane was essentially identical with that in methanol (the 254 nm rotation at +45.0° decreased to 0.76 of its −15.0° value). Unfortunately the low solubility of the other biphenyls in *n*-octane precluded further studies in this solvent.

The data indicate that large reversible changes in rotation occur. In the case of Id, for example, the rotation decreases by more than one-third upon going from −15 to +45°. Such a phenomenon strongly suggests that there be a

Table I. Variation of ORD Intensity with Temperature (methanol solution)[a]

Compound	Temp (°C)	λ_{max}, nm	Relative rotation[b]
Ib	−15.0	254	1.00 ± 0.02
	+14.5		0.84
	+45.0		0.75
Ic	−15.0	261	1.00
	+15.0		0.88
	+45.0		0.76
Id	−14.0	258	1.00
	+14.0		0.86
	+45.0		0.64
Ie	−15.0	255	1.00
	+15.0		0.93
	+45.0		0.85
X	−15.0	263	1.00
	+14.8		0.94
	+45.0		0.91

[a] No appreciable changes in λ_{max} were observed upon change in temperature. [b] Corrected for expansion.

Table II. Variation of the Methyl Proton Resonances of 2,2′-Dimethyl-6,6′-dinitrobiphenyl (Ib) with Temperature

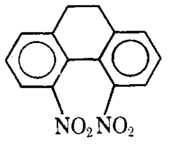
Temp (°C)[a]	Solvent	(Hz)[b]
55	Chlorobenzene	27.0 ± 0.1
41		28.2
34		28.3
28	Methylene chloride	23.7
2		24.5
−35		25.7
−48		26.0

[a] Calibrated from ethylene glycol and methanol resonances. [b] Downfield from the methyl resonance of internal toluene.

net conversion to a species of opposite rotation upon heating.

The proton nmr of Ib, provides some further conformation of this explanation. The chemical shifts of the methyl protons of Ib (measured versus internal toluene) vary slightly with temperature as would be expected for an increase in IIb/IIIb with increasing temperature (see Table II).

The temperature dependence of the ORD spectra of 4,5-dinitro,9,10-dihydrophenanthrene[7] (X) was measured for comparison. Due to its dimethylene bridge, the 90° barrier VIII should not be accessible, effectively preventing equilibration of conformations analogous to II and III. As the data of Table I indicate, the temperature dependence of the rotation of X is significantly less than for Ib-c.



X

If optically active biphenyls have a single minimum between $\phi = 0$ and 180° the observed temperature dependence might be attributed to population of excited torsional vibrational modes about the C_1–C_1 bond. The observed decrease in rotation for Ib-e upon such a small increase in temperature would probably require extensive population of excited modes that were so anharmonic as to change the sign of the net rotation for these molecules but not for X. Upon consideration of the ORD and NMR evidence we feel the most likely conclusion to be that, even those biphenyls with fairly bulky groups on the ortho positions exist in pairs of disastereomeric conformations for each enantiomer in solution. These conformations are analogous to those reported for biphenyl, itself, in the gas phase.

Table III. Specific Rotation (methanol, 45°) at Peaks and Troughs[a]

Compound	Specific rotation (wavelength in nm)
Ib[b]	+13,000 (254), +3200 (280),[c] −880 (303), +590 (322), −2900 (~400)
Ic[b]	+450 (261), 300 (297),[c] −150 (370)
Id[b]	+670 (258), +10 (304), +66 (325), −130 (380)
Ie[b]	−4100 (255), −470 (304), −740 (316), +280 (364), −280 (445)
X	−18,000 (263), −7900 (285), −11,000 (300), +5000 (~350), −250 (445)

[a] The samples used were not necessarily optically pure. These values are nevertheless included upon the suggestion of a referee. [b] Specific rotation for these compounds under other conditions can be found in ref 5b. [c] Indicates shoulder.

Some useful analogies to the present work are provided by a recent study of 2,2-dithienyl which concluded that this molecule exists in two equilibrating conformations, reported to be the planar s-cis and s-trans,[8] the correlation of specific rotation with conformation in methyl 2-deoxy- α-L- and 3-deoxy-β-L-*erythro*-pentopyranosides,[9] and the correlation of rotation with temperature for di-5-(2′-deoxyuridilyl) disulfides.[10]

The biphenyls (Ib-e) were all prepared by published procedures.[11] The 2,2′-dinitrodiphenic acid was resolved with α-methylbenzylamine and 2,2′-dimethyl,-6,6′-dinitrobiphenyl was prepared from the resolved acid. Satisfactory spectra and elemental analyses were obtained for all compounds.

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The Mechanism of Action of Vitamin B_{12}

Sir:

Vitamin B_{12}, in the form of its coenzyme, is an obligatory cofactor in ten, known enzyme-catalyzed rearrangement reactions.[1] Of the ten, three are carbon-skeleton rearrangement reactions. They are the reversible interconversions β-methylasparate ⇄ glutamate[2] (eq 1), methylmalonyl-CoA ⇄ succinyl-CoA[3] (eq 2), and β-methylitaconate ⇄ α-methyleneglutarate[4] (eq 3).