Tetrahedron. Vol. 32, pp. 2915 to 2922. Pergamon Press 1976. Printed in Great Britian

A THEORETICAL STUDY OF CONFIGURATIONAL INVERSION IN 1,1'-BINAPHTHYL BY MOLECULAR MECHANICS

ROBERT E. CARTER* and TOMMY LILJEFORS*
Organic Chemistry 2 and 1, Chemical Center, University of Lund, 220 07 Lund, Sweden

(*Received in UK 27 January 1976; Accepted for publication 6 July 1976*)

Abstract—The molecular mechanics method has been applied to the study of various pathways and transition states for the configurational inversion of 1,1'-binaphthyl. The preferred pathway is found to be one on the *anti* ("*trans*") side involving one point of H · · · H nonbonded contact in each of two identical transition states, separated by a very shallow minimum. Very satisfactory agreement with available experimental values for the enthalpy of activation is achieved.

The details of the process of configurational inversion in optically active, 1,1'-binaphthyl and its derivatives have hitherto not been satisfactorily elucidated, although rather extensive experimental studies have been carried out, especially by Harris *et al.*[1] including an attempt (by Cooke and Harris[1b]) to delineate various inversion paths on the background of the experimental results. The role of "ground-state distortions" in the substituted compounds (the 8,8'-series in particular) as an important factor in the determination of the height of the barrier to inversion has often been emphasized.[1] It has not been possible to unequivocally distinguish between one- and two-step inversion paths, but Cooke and Harris[1b] have suggested that 8,8'-disubstituted derivatives undergo inversion in two discrete steps, one for each pair of opposing atoms, whereas for 2,2'-disubstituted derivatives, inversion proceeds in one step. Subsequently, an attempt was made by Carter and Dahlgren[2] to obtain a piece of detailed information about the structure of the transition state in connection with a study of the steric kinetic deuterium isotope effect in the racemization of (−)-1,1'-binaphthyl-2,2'-d_2. On the basis of the size of the isotope effect, in conjunction with the equations of Bartell[3,4] relating the isotopic difference in activation energy to the second and fourth derivatives of a nonbonded H · · · H potential function, the H · · · H nonbonded distance in the transition state was estimated to be "about 2.0 Å".

The availability of the molecular mechanics computer program developed by Allinger and his group,[5] which includes a very efficient minimization routine, and can take into account p–π conjugation in, e.g. aromatic systems,[5b,e] aroused our interest in attempting to perform a careful calculation of molecular conformations along various conceivable paths for configurational inversion in 1,1'-binaphthyl. Our main objective was to gain insight into the details of the inversion process, and we felt that the application of the full relaxation molecular mechanics method with the Allinger program would enable us to do so, especially since the reliability of the program for calculations on aromatic molecules is well documented.[5b,e] Previously, calculations had been carried out by Gamba *et al.*[6] using the "molecules in molecules" approach[7] and Hückel π-energy calculations, together with nonbonded potential functions and a stretching function for the inter-ring bond, to investigate the initial-state equilibrium conformation, and total energies were derived for ring-ring dihedral angles between about 60 and 120°. A shallow minimum was found to extend about 15° on either side of 90°. The only other calculation on binaphthyl in the literature is apparently the work of Dashevsky and Kitaygorodsky,[8] who found an equilibrium dihedral angle of 62°, using their molecular mechanics method.[9] It is not possible to allow for relaxation with respect to all of the available degrees of freedom (ring bending, in particular) with the previously employed computational methods, and consequently it was previously unfeasible to calculate realistic transition-state energies in the binaphthyl system. As will be described below, our results provide a picture of the initial state similar to that reported by Gamba *et al.*,[6] and furthermore, the experimentally observed barrier to inversion is well reproduced by our calculations on various transition-state conformations. A point of interest is that the naphthalene rings are found to be quite flexible and capable of considerable distortion from planarity without undue expenditure of energy. (The flexibility of aromatic ring systems has previously been commented upon by, e.g. Wynberg *et al.*,[10] and by Allinger, Sprague and Liljefors.[5e])

Method of calculation. The main feature of the force field method developed by Allinger *et al.* for the calculation of the structures and energies of hydrocarbons with delocalized electronic systems[5b,e] is the incorporation of a quantum mechanical π-system calculation (VESCF) in the energy minimization sequence. The VESCF method provides bond orders, from which stretching and torsional force constants are calculated. The torsional force constants were evaluated according to the modified equations given in Ref. 5*e*. Using this modification, the deformations of the benzene ring in [n]paracyclophanes could be adequately reproduced.[5e] This is of great importance for the present work, since the naphthalene residues in binaphthyl would be expected to become distorted along the pathways to inversion.

Allinger's 1973 force field[5a] was used throughout the calculations. The parameters for the conjugated system are summarized in Table 1, and it should be noted that no parameter fitting was undertaken in connection with this work.

Local minima in the potential energy, corresponding to stable conformers, were found by allowing the energy of several different trial structures to minimize in an unconstrained fashion with respect to all degrees of freedom.

Table 1. Force field (Allinger 1973)[5a]

van der Waals Constants

$E_v = -2.25\ \varepsilon(r^*/r)^6 + 8.28\cdot10^5\ \varepsilon\ \exp(-r/0.0736r^*)$

Atom	r^* (Å)	ε (kcal/mol)
Csp^2	1.85	0.030
H	1.50	0.063

For van der Waals calculations the electron cloud around H is centered 0.925 of the distance along the C-H bond.

Stretching Constants

$E_s = 71.94\ k_s(l-l_o)^2(1 + (C_s(l-l_o))\quad C_s = -2.00$

Bond	l_o (Å)	k_s (mdyn/Å)
Csp^2-Csp^2	1.334[a]	9.6[a]
Csp^2-H	1.090	4.6

Bending Constants

$E_b = 0.021914 \cdot k_b(\theta-\theta_o)^2\ (1 + C_f\ (\theta-\theta_o))\quad C_f = -0.006$

Angle	θ_o (deg)	k_o (mdyn Å/rad^2)
Csp^2-Csp^2-Csp^2	120.0	0.60
Csp^2-Csp^2-H	120.0	0.24
out-of-plane	0.0	0.05

Stretch-bend Constants

$E_{sb} = 2.51124\ k_{sb}\ (\theta-\theta_o)[(l_1-l_o) + (l_2-l_o)]$

Atoms	k_{sb}
C-C-C	0.12
C-C-H	0.04

Torsional Constants

$E_t = V_1/2\ (1 + \cos(\omega)) + V_2/2(1-\cos(2\omega)) + V_3/2(1+\cos(3\omega))$

Angle	V_1	V_2	V_3 (kcal/mol)
Csp^2-Csp^2-Csp^2-Csp^2	0.0	16.25[a]	0.80
Csp^2-Csp^2-Csp^2-H	0.0	16.25[a]	0.0
H-Csp^2-Csp^2-H	0.0	16.25[a]	0.0

Torsion-bend Constants

$E_{tb} = k_{tb}\ (1-\cos(2\omega))[(\theta_1-\theta_o) + (\theta_2-\theta_o)]$

$k_{tb} = -0.0110$ for C-C-C-C, zero otherwise

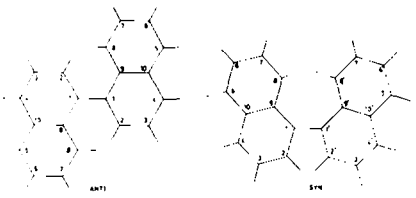
[a] These values correspond to a π-bond order equal to one. They are modified in the minimization sequence according to the procedures described in refs. 5b and 5e.

Pathways connecting local minima were calculated using an approach similar to that previously described by Wilberg and Boyd.[11] A one-fold torsional function,

$$V = (V_1/2)(1-\cos(\omega-\theta))$$

was used in the calculations of derivatives in the energy minimization sequence for a dihedral angle effecting the rotation about the pivot bond C_1–C_1'. This function is minimized by varying ω, and by assigning a large positive value to V_1, making the potential stiff, the torsional energy will have a minimum at a chosen value, θ, and the dihedral angle will remain at this value throughout the minimization of all other degrees of freedom. Pathways between local minima can now be calculated by allowing θ to assume a series of values, "driving" the dihedral angle to effect the rotation.

To make the discussion of pathways to inversion as complete as possible, we have investigated passages on the *syn* side and the *anti* side involving one or two points of H···H nonbonded contact (one or two H atoms passing each other in the transition state; cf. discussions in Refs 1*a* and 1*b*). In order to be able to do this without



using unreasonable amounts of computer time, we have in certain cases used symmetry restrictions, which will be discussed below in connection with the pertinent calculations. In principle, there are four dihedral angles that may be used as "driving angles": C_9–C_1–$C_{1'}$–$C_{9'}$, C_2–C_1–$C_{1'}$–$C_{9'}$, C_9–C_1–$C_{1'}$–$C_{2'}$, C_2–C_1–$C_{1'}$–$C_{2'}$. (In the presence of symmetry restrictions, some of these angles will be identical.) Only one driving angle has been varied at a time, and as will be discussed below, the appropriate choice of an angle in a given case is not without importance. Each dihedral angle may be regarded as representing different "rotational" reaction coordinates (although the true reaction coordinates are much more complex), and may thus lead to different transition states.

The pathways that we may calculate by means of this approach are characterized by minimal distortions of the naphthalene ring systems along the chosen "rotational" reaction coordinate. The distortions are mainly due to H···H repulsions hindering the inversion of the molecule. Calculations of pathways along combined "rotation-distortion" reaction coordinates would require some structural element giving rise to the distortion of the naphthalene units to be incremented in a stepwise manner. However, these distortions are not a simple function of any recognizable single structural element. The pathways we calculate are thus *not necessarily* the "best" ones for the inversion process, but the calculated pathways and alternative transition states provide a basis for a discussion of the details of the inversion.

RESULTS AND DISCUSSION

Preliminary calculations. The structure of naphthalene has been determined by both electron diffraction[12] and X-ray crystallographic methods,[13] and it was of interest to calculate this structure with the Allinger program for comparison with the experimental data in order to reconfirm the reliability of the program on a molecule of utmost relevance to the present work.

The calculated bond lengths and angles are in agreement with the available experimental results[12,13] within the limits of error (taken as 3 times the reported standard deviations), as shown by the data summarized in Table 2. It should be noted that the most adequate comparison is that between the electron-diffraction (gas phase) data and our calculated values.

Another relevant molecule for our purposes is biphenyl, the equilibrium conformation of which has previously been calculated by Allinger and Sprague,[5b] as well as by several other workers.[14] The structure in the gas phase is reported to be non-planar,[15] with a dihedral angle of 41.6°, while an essentially planar conformation has been found in the crystal.[16] The force field used in this work is an updated version (see Table 1) of that used by Allinger and Sprague in Ref. 5*b*, and thus we have recalculated the conformational energy as a function of the dihedral angle in order to determine the equilibrium conformation for comparison with experiment, and to estimate the barrier to internal rotation for comparison with calculations by molecular orbital methods. We find a shallow minimum at approximately 40°, in good agreement with experiment, and the barrier to rotation is calculated to be 3.4 kcal/mol. Other theoretical values for the barrier are ≤4.5 kcal/mol[14d] and "2–4 kcal/mol".[14b] The length of the inter-ring bond is calculated to be 1.500 Å in the planar molecule and 1.493 Å at a dihedral angle of 40°. These values are in excellent agreement with available crystallographic (1.497,[16a] 1.506,[16b] 1.507[16c] Å) and electron-diffraction (1.489 ± 0.0075 Å[15]) data, respectively. The inter-ring bond distance is calculated to be 1.519 Å at a dihedral angle of 90°, which may be compared with a value of 1.515 ± 0.0015 Å, obtained by electron diffraction[17] on hexaphenylbenzene. In this molecule, all six phenyl rings are twisted 90° with respect to the plane of the benzene ring. In the light of our results on naphthalene and biphenyl, we may approach the calculation of the initial-state equilibrium conformation of 1,1'-binaphthyl with some confidence.

Initial-state binaphthyl conformation. 1,1'-Binaphthyl exists in two crystalline modifications, A and B, the first of which has been deduced to be in an *anti* ("*trans*")

Table 2. Comparison between experimental and calculated bond lengths and bond angles in naphthalene (Bond lengths in Å, angles in deg.)

Bonds	X-ray[13,a]	Electron diffraction[12,b]	Calculated
C_1-C_2	1.364	1.371	1.378
C_2-C_3	1.415	1.412	1.421
C_1-C_9	1.421	1.422	1.428
C_9-C_{10}	1.418	1.420	1.413
Bond angles			
C_1-C_2-C_3	120.60	120.82	120.4
C_2-C_1-C_9	120.18	119.76	120.2
C_1-C_9-C_{10}	119.13	119.42	119.4
C_1-C_9-C_8	121.75	121.16	121.2

[a] Average standard deviations are approximately 0.005 Å for bonds and 0.25° for bond angles.[13]

[b] Standard deviation for C_2-C_3 0.014 Å, otherwise 0.004–0.009 Å for bonds and 0.22° for bond angles.[12]

Table 3. Comparison between experimental and calculated bond lengths and bond angles in 1,1'-binaphthyl

Bonds	X-ray (Å)[19,a]	Calc. (Å)	Angles	X-ray (°)[19,a]	Calc. (°)
C_1-$C_{1'}$	1.475	1.519	C_1-C_2-C_3	122.0	120.6
C_1-C_2	1.365	1.377	C_2-C_3-C_4	119.8	120.3
C_2-C_3	1.404	1.421	C_3-C_4-C_{10}	120.8	120.2
C_3-C_4	1.360	1.378	C_4-C_{10}-C_9	119.3	119.4
C_4-C_{10}	1.413	1.428	C_4-C_{10}-C_5	122.4	121.1
C_5-C_{10}	1.414	1.427	C_5-C_{10}-C_9	118.2	119.5
C_5-C_6	1.346	1.379	C_6-C_5-C_{10}	122.3	120.3
C_6-C_7	1.404	1.420	C_5-C_6-C_7	119.8	120.2
C_7-C_8	1.359	1.379	C_6-C_7-C_8	119.7	120.3
C_8-C_9	1.413	1.427	C_7-C_8-C_9	122.1	120.5
C_9-C_{10}	1.416	1.413	C_8-C_9-C_{10}	117.9	119.1
C_1-C_9	1.433	1.430	C_1-C_9-C_8	123.1	121.5
			C_1-C_9-C_{10}	119.0	119.4
			C_2-C_1-C_9	119.0	120.0

[a] Standard deviations 0.0029-0.0050 Å for bonds and 0.19-0.27° for bond angles.[19]

configuration.[18] The crystal structure of the B modification was investigated by Kerr and Robertson,[19] who report it to exhibit a *syn* ("*cis*") configuration with a dihedral angle (θ) of 68°. Our calculated binaphthyl structure has an energy minimum at $\theta = 88.6°$, but the bottom of the potential well is *very* shallow, and within ±25° of the minimum, the energy changes ≤0.3 kcal/mol. The existence of more than one crystalline form is understandable in terms of this shallow potential well. The value of the dihedral angle reported by LeFèvre *et al.*[20] on the basis of Kerr constant measurements extrapolated to infinite dilution in benzene solution, is 48°, which certainly appears to be an underestimate. Akimoto *et al.*[21] have determined the crystal structure of a binaphthyl derivative, (+) - 2,2' - dihydroxy - 1,1' - binaphthyl - 3,3' - dicarboxylic acid dimethyl ester, which apparently also exists in the *syn* form, with a dihedral angle of 77°.

The length of the 1,1'-bond reported by Kerr and Robertson[19] (1.475 ± 0.005 Å) is considerably shorter than our value of 1.519 Å for the minimum energy conformation. At $\theta = 65°$, we calculate a length of 1.499 Å for this bond, which is outside of the reported[19] experimental error, even if the error is multiplied by a factor of three to reach 99% confidence limits. In the calculations reported by Gamba *et al.*[6] this bond distance was found to be 1.49 Å at the energy minimum. The same value was found[6] for 1- and 2-phenylnaphthalene, and for 1,2'- and 2,2'-binaphthyl. Kerr and Robertson[19] compare their result with values calculated by molecular orbital or valence bond methods on the basis of bond-order—bond-length reltionships, and acceptable agreement is found. However, such methods of calculations do not take into account the effect of nonbonded repulsions, and as a consequence quite naturally lead to a shortened 1,1'-bond. Part of the difference between our (gas-phase) value and that of Kerr and Robertson[19] may of course be due to crystal packing forces, but such effects are not adequate to explain the entire discrepancy.

†A third possibility is the C_2-C_1-$C_{1'}$-$C_{9'}$ angle, but it was found that under the assumption of C_2 symmetry, driving this angle made angles (i) and (ii) interdependent, thus leading to a high energy since the structure is forced to be unnecessarily stiff.

The calculated structure of each naphthyl unit is quite similar to that of naphthalene itself, except that the rings are not strictly planar (but nearly so), with out-of-plane bending <0.1° for all carbon atoms. This feature is also found in the crystal structure,[19] but the deviations from planarity are apparently somewhat larger.

Possible inversion pathways. Several different pathways for the configurational inversion of 1,1'-binaphthyl are a priori conceivable, viz. rotation toward the *syn*- or *anti*-side in conjunction with simultaneous (2 H · · · H nonbonded points of contact) or more or less stepwise (one point of cantact) passage of the pertinent protons in the transition state(s). Cooke and Harris[1b,d] assume, at least for the substituted compounds, that passage occurs exclusively on the *anti* side, and our calculations provide ample justification for this assumption. Reasonable transition states on the *syn* side are found to be at least 10 kcal/mol higher in energy than corresponding transition states on the *anti* side.

syn *Inversion paths.* In order to economize on computer time, the pathways with one point of H · · · H nonbonded contact were calculated under the reasonable (but not necessary) assumption that the molecule maintains C_2 symmetry during the inversion process. We found that somewhat different potential energy paths were followed depending upon the "driving" dihedral angle, i.e. whether (i) the C_9-C_1-$C_{1'}$-$C_{9'}$ angle or (ii) the $C_{2'}$-$C_{1'}$-C_1-C_2 angle was incremented to achieve the rotation about the C_1-$C_{1'}$ bond.† In case (i), protons H_2 and $H_{2'}$ pass each other at a C_9-C_1-$C_{1'}$-$C_{9'}$ angle of ca. 30°; the energy at this point is 22.5 kcal/mol above the initial state. When the driving angle reaches a value of ca. 72°, the other (III, Fig. 1) passage (H_8-$H_{8'}$) occurs close to an energy of 34.2 kcal/mol and an H_8 · · $H_{8'}$ nonbonded distance of 2.156 Å. Driving angle (ii) leads to closest contact (passage) for H_2-$H_{2'}$ at 0°, and at a much lower energy (11.3 kcal/mol) than that obtained in case (i). (The H_2 · · · $H_{2'}$ distance is 2.191 Å at this point; II, Figs. 1 and 3). Continuation along the path ordained by (ii) would lead to the passage of H_8 and $H_{8'}$ at an energy much higher than the value of 34.2 kcal/mol calculated in case (i). No attempt was made to force H_8 and $H_{8'}$ past each other by driving angle (ii), since we presume that the best path on

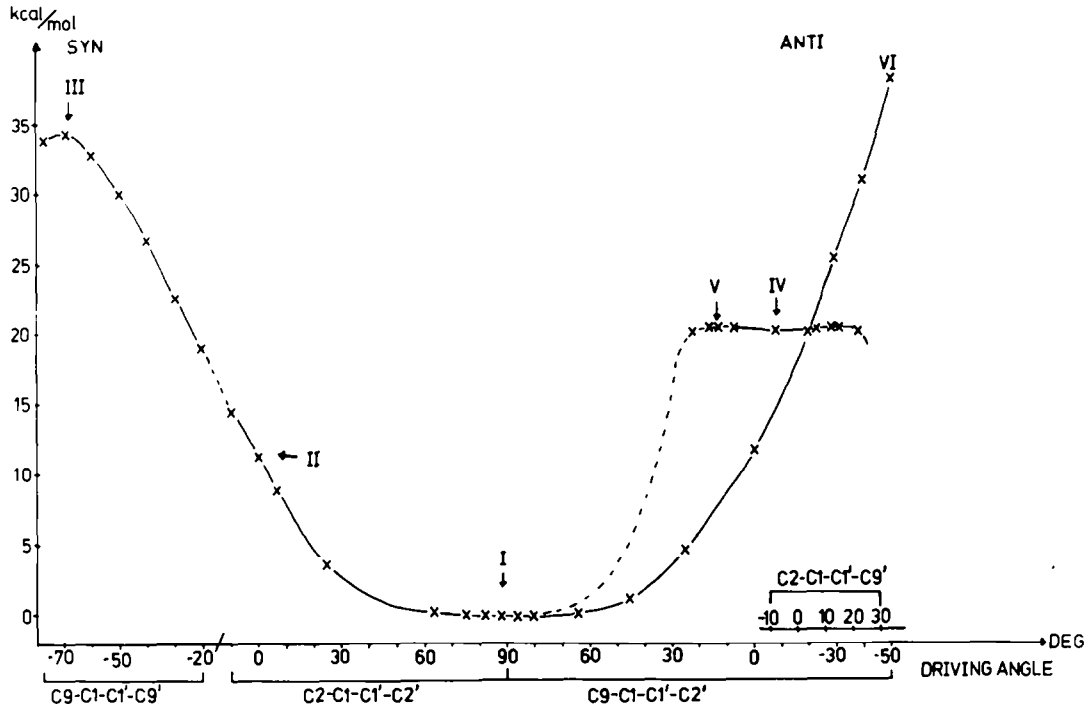


Fig. 1. Calculated energies vs driving angle for 1,1'-binaphthyl assuming "one point of H · · · H nonbonded contact" pathways. (The dashed portions of the curve are connection lines between calculated parts of the potential surface).

the *syn* side is a composite of the pathways represented by (i) and (ii) (Fig. 1). This would imply crossing from one "rotational" reaction coordinate to another on the potential energy surface during the course of the inversion process.

Ring bending is obviously a very important relaxation mode for *syn* side inversion, leading to gross distortions from planarity, as shown in a stereoview of a conformation representing the transition state (at 34.2 kcal/mol) in Fig. 3 (III).

A point of interest is that there is no local minimum between the two proton-proton passages, in contrast to the situation on the *anti* side (one point of contact) to be discussed in detail below. Thus, even though the lowest-energy passage is at 11.3 kcal/mol (II), the total barrier to inversion along a "rotation-minimal distortion" reaction coordinate would be 34.2 kcal/mol, which is more than 10 kcal/mol higher than the experimentally observed $\Delta H^{\neq}$ (21.5 ± 0.2 kcal/mol;[2] 21.9 kcal/mol[1b]).

An inversion pathway on the *syn* side involving two points of contact could not be mapped out by only following a simple "rotational" reaction coordinate. In all such attempts the system relaxed to the one point of contact pathway. Instead, we have calculated the energies of various transition-state models, of which one with C_s symmetry was found to have the lowest energy, viz. 36.6 kcal/mol (VII, Figs 2 and 3). In this transition state, the $H_2 \cdots H_{2'}$ and $H_8 \cdots H_{8'}$ nonbonded distances are 2.146 Å and 2.116 Å, respectively.† This energy is only 2.4 Kcal/mol higher than that found for one point of contact, and once again illustrates the way in which ring bending distortions can "absorb" excess energy. It is clear that any pathway leading to this transition state must involve a combination of "rotation" and "distortion" reaction coordinates.

In view of the large differences between the calculated inversion barriers on the *syn* side and the experimental value, we may eliminate the *syn* side from further consideration, and proceed to a description of pathways on the *anti* side, one of which will be seen to emulate the observed barrier quite satisfactorily.

anti *Inversion pathways.* Harris *et al.*[1a,b] have discussed inversion on the *anti* side, with specific reference to 8,8'- and 2,2'-disubstituted binaphthyls. "Mesoid" and "racemoid" inversion pathways are described, which differ in the relative configurations of the naphthyl residues, and, most significant from our point of view, differ with respect to the number of points of nonbonded contact in the transition state(s). The "mesoid" path involves one point of contact in each of two identical transition states, separated by an intermediate with a center of symmetry (C_i), whereas the "racemoid" path involves two points of contact in a single transition state. The 8,8'-disubstituted compounds are assumed to suffer more initial-state strain than the 2,2'-analogs, as a result of which the former are in general more readily racemized than the latter. Our calculations clearly indicate that the transition state for the path with two points of contact, which corresponds to but is not identical with the "racemoid" transition state of Harris *et al.*[1] is found to lie more than 14 kcal/mol above the transition state(s) for the alternative "mesoid" path.

Conformational energies along the inversion pathway characterized by two simultaneous H · · · H passages in the transition state were calculated by driving the C_2–C_1–$C_{1'}$–$C_{2'}$ angle under the assumption of C_2 symmetry. We have no reason to believe that this is an unnecessarily severe symmetry restriction. In this case, the "true"

†All H · · · H nonbonded distances reported in this paper are between the centres of electron density of the pertinent C–H bonds, i.e. 0.925 X (C–H bond distance).[5a]

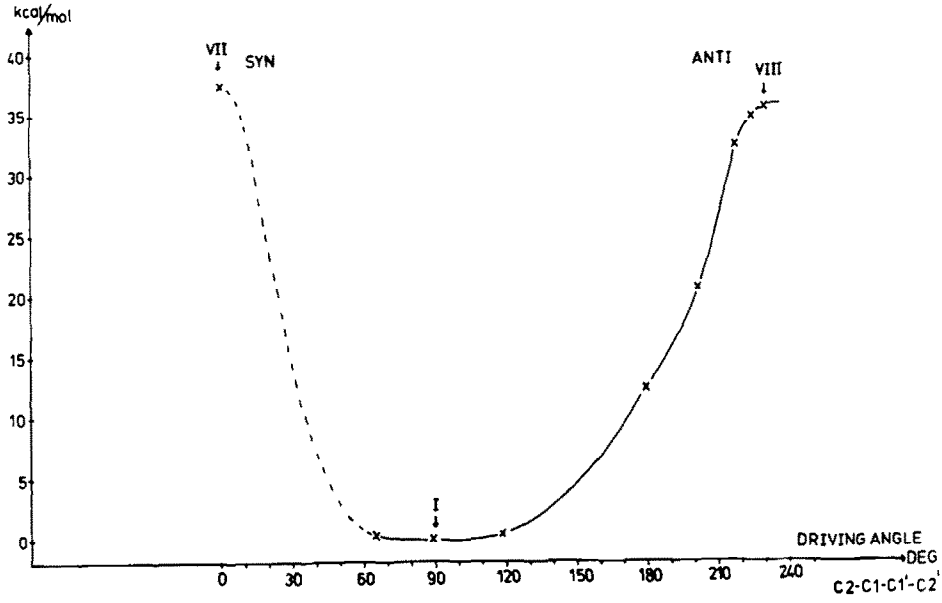


Fig. 2. Calculated energies vs driving angle for 1,1'-binaphthyl assuming "two points of H · · · H nonbonded contact" pathways. (The dashed portion of the curve is a connection line between calculated parts of the potential surface).

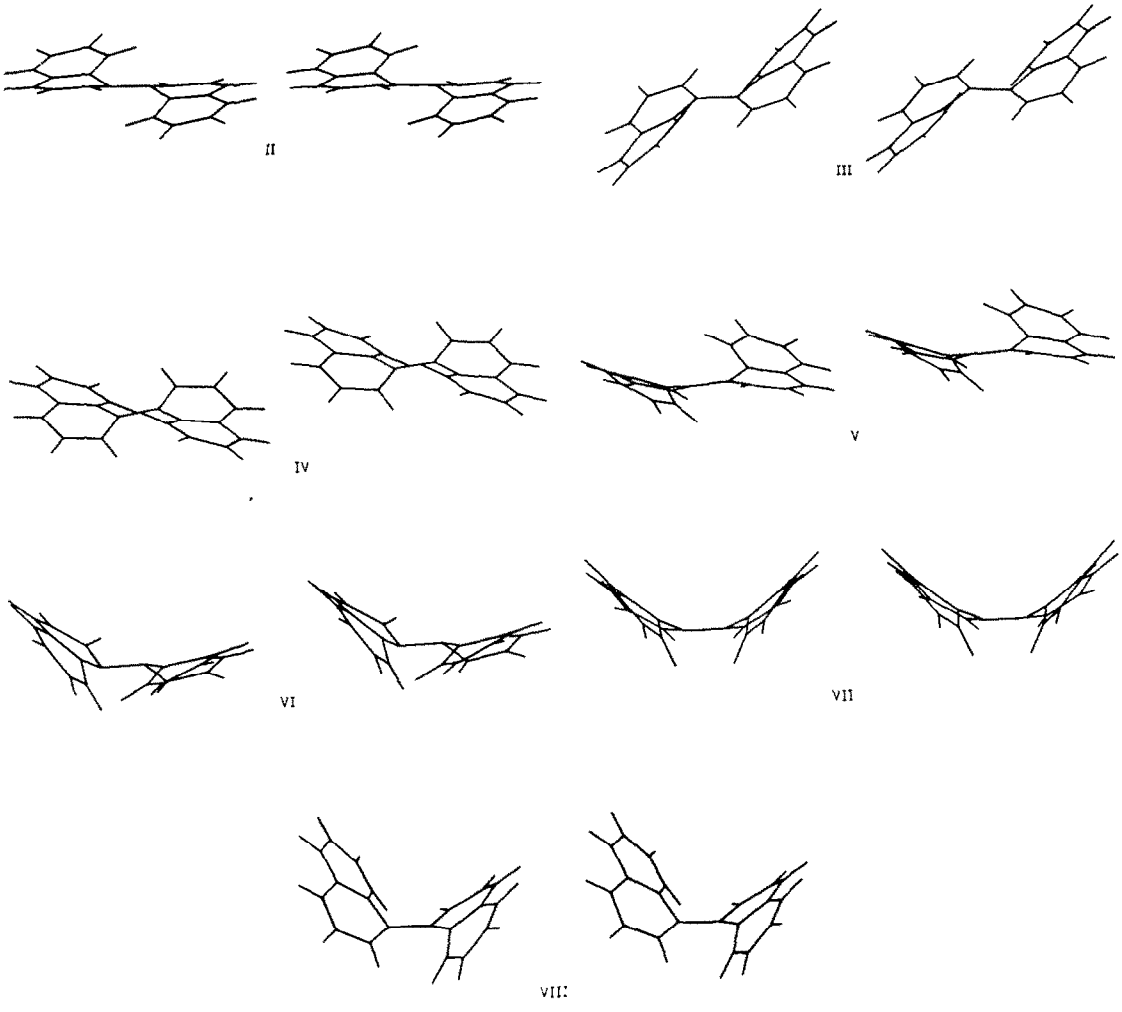
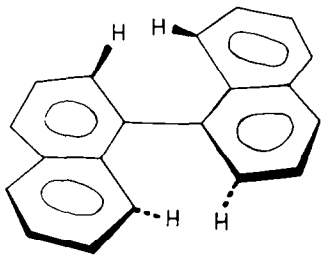


Fig. 3. Calculated conformations of 1,1'-binaphthyl along various inversion pathways.

transition state was not actually reached in the computations, since this could only be done by changing the driving angle in a very small increments, which would have required an inordinate amount of computer time. At a driving angle of *ca* 232°, the H · · · H nonbonded distance is 2.129 Å, and the calculated energy is 34.7 kcal/mol (see VIII, Figs 2 and 3), which is certainly no more than 0.2 kcal/mol below the "true" transition state along this reaction coordinate, and about 13 kcal/mol above the experimentally observed inversion barrier.[1b,2] Along a combined "rotation-distortion" reaction coordinate there is a possibility for the molecule to reach a transition state of C_i symmetry with two points of contact. The energy of such a transition state could however not be obtained, since any trial structure of C_i symmetry would minimize to a local minimum on the "mesoid" pathway described below. (Nonetheless, this result shows



that the energy of this transition state is higher than that of the local minimum at 20.2 kcal/mol). The C_i transition-state energy is probably also higher than that of the C_2 transition state, since in the C_i case, alleviation of the repulsion between one of the pairs of H's in contact (by out-of-plane ring bending) will intensify the repulsion between the other pair. In the C_2 transition state, out-of-plane bending at C_1 and $C_{1'}$ relieves repulsion of both pairs of hydrogens in contact, thus providing a possibility for relaxation which is not available in the C_i case.

The calculated energy for the C_2 transition state (34.7 kcal/mol) is of the same order of magnitude as that found for inversion on the *syn* side, and consequently the "racemoid" path may also be eliminated from consideration.

As mentioned above, a local minimum on the anti side, with C_i symmetry, was found 20.2 kcal/mol above the initial-state minimum, corresponding to a situation in which H_2 and $H_{8'}$ (*or* H_8 and $H_{2'}$; IV, Figs 1 and 3), have passed each other. The best path along a rotational reaction coordinate connecting this local minimum with the initial-state minimum was obtained by driving the C_9–C_1–$C_{1'}$–$C_{2'}$ dihedral angle (without symmetry restrictions) through a transition state only 0.2 kcal/mol above the local minimum (V, Fig. 3), making the potential in this region extremely shallow (see IV-V, Fig. 1). (This is of course equivalent to driving the C_2–C_1–$C_{1'}$–$C_{9'}$ angle in the opposite sense of rotation.) This could be a close approximation to the preferred pathway for inversion, since any alternative pathway involving an additional "distortion" reaction coordinate must have a transition state energy ≥ 20.2 kcal/mol. This pathway is similar to the "mesoid" route discussed by Harris *et al.*[1a,b] The transition-state energy of 20.4 kcal/mol is in very satisfactory agreement with the available experimental data: $\Delta H^{\neq} = 21.5 \pm 0.2$[2] and 21.9[1b] kcal/mol in dimethylformamide solution. Colter and Clemens[22] report $\Delta H^{\neq}$ values ranging from 21.6 to 22.7 kcal/mol, depending upon the solvent, but since these values were apparently derived from rate constant determinations at only two temperatures, it is not possible to estimate the experimental error limits and thus to judge the significance of this 1 kcal/mol difference.

Interestingly enough, the transition state does not correspond to the shortest H · · · H nonbonded distance, primarily because as the transition state is passed (from the local minimum) and protons H_8 and $H_{2'}$ approach each other, the increased van der Waals repulsion is compensated by the release of distortions (and consequent increase in planarity) on the opposite side of the molecule. This is also the reason for the shallowness of the potential in the region of the local minimum. In the transition state, the $H_8 \cdots H_{2'}$ distance is 2.147 Å, whereas the closest approach of these two protons, 2.116 Å, occurs 0.2 kcal/mol below the transition state.

Isotope effect. The isotopic difference in activation energy in the racemization of 1,1'-binaphthyl-2,2'-d_2 was taken to be ≃100 cal/mol by Carter and Dahlgren[2] on the basis of the measured $\Delta\Delta G^{\neq}$ ($=\Delta G_H^{\neq} - \Delta G_D^{\neq}$) values and the assumption[2,23] that $\Delta\Delta S^{\neq} = 0$. Using the equations of Bartell[3,4] and the H · · · H nonbonded potential function incorporated into Allinger's program[5] a value of 96 cal/mol for the isotopic energy difference may be calculated for the pathway with two points of contact, in gratifying agreement with the experimental estimate.[2]

CONCLUSIONS

In our opinion, the calculations show quite conclusively that the "mesoid" path is the preferred route for configurational inversion in 1,1'-binaphthyl. The exact nature of the pathway from the initial state to the calculated transition state is less clear, as it cannot be discerned by driving a dihedral angle alone. Such an approach leads to a higher energy transition state (>35 kcal/mol; VI, Figs 1 and 3), and once again a combination of "rotation" and "distortion" reaction coordinates must be assumed.

The finer details of our results reflect of course the parametrization of the Allinger Program, but its previous successes with aromatic hydrocarbons[5b,c] and our own test runs on naphthalene and biphenyl, as well as the agreement between calculated and experimental energy barriers in binaphthyl, provide a rather firm basis for confidence in the utility of this program for calculations of initial- and transition-state structures and energies in flexible aromatic molecules.

Further calculations are in progress in order to elucidate the nature of the inversion pathway(s) in 8,8'- and 2,2'-disubstituted binaphthyls, since the present results suggest that paths with two points of nonbonded contact will *in general* be of significantly higher energy than corresponding "one-point" paths.

Acknowledgements—We wish to acknowledge our indebtedness to Prof. Norman L. Allinger, University of Georgia, for placing his molecular mechanics program at our disposal. This work was supported in part by the Swedish Natural Science Research Council.

REFERENCES

[1a] M. M. Harris and Cheung King Ling, *Chem. Ind.* 1378 (1962); [b] A. S. Cooke and M. M. Harris, *J. Chem. Soc.* 2365 (1963); [c] Y. Badar, A. S. Cooke and M. M. Harris, *Ibid.* 1412 (1965); [d] A. S. Cooke and M. M. Harris, *Ibid.* (C) 988 (1967); [e] M. M. Harris, R. Z. Mazengo and A. S. Cooke, *Ibid.* (C) 2575 (1967).

[2] R. E. Carter and L. Dahlgren, *Acta chem. Scand.* 23, 504 (1969).

[3]L. S. Bartell, *J. Am. Chem. Soc.* 83, 3567 (1961); *Iowa State J. Sci.* **36**, 137 (1961); *Tetrahedron Letters* 13 (1960).
[4]L. Melander and R. E. Carter, *Acta Chem. Scand.* **18**, 1138 (1964).
[5a] D. H. Wertz and N. L. Allinger, *Tetrahedron* **30**, 1579 (1974); [b] N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.* **95**, 3893 (1973); [c] N. L. Allinger and J. T. Sprague, *Ibid.* **94**, 5734 (1972); [d] N. L. Allinger, M. T. Tribble, M. A. Miller and D. H. Wertz, *Ibid.* **93**, 1637 (1971); [e] N. L. Allinger, J. T. Sprague and T. Liljefors, *Ibid.* **96**, 5100 (1974); [f] T. Liljefors and N. L. Allinger, *Ibid.* **98**, 2745 (1976).
[6]A. Gamba, E. Rusconi and M. Simonetta, *Tetrahedron* **26**, 871 (1970).
[7]H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc. LXVII*, **7-A**, 40 (1955).
[8]V. G. Dashevsky and A. I. Kitaygorodsky, *Theor. Eksp. Khim.* **3**, 43 (1967).
[9a] A. I. Kitaygorodsky, *Tetrahedron* **14**, 230 (1961); [b] A. I. Kitaygorodsky and V. G. Dashevsky, *Theor. Eksp. Khim.* **3**, 35 (1967); A. I. Kitaygorodsky, *Molecular Crystals and Molecules*, Chap. VII. Academic Press, New York and London (1973).
[10]H. Wynberg, W. C. Nieuwpoort and H. T. Jonkman, *Tetrahedron Letters* 4623 (1973).
[11]K. B. Wiberg and R. H. Boyd, *J. Am. Chem. Soc.* **94**, 8426 (1972).
[12]A. Almenningen, O. Bastiansen and F. Dyvik, *Acta Cryst.* **14**, 1056 (1961).
[13]D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.* **A258**, 270 (1960).
[14a] F. J. Adrian, *J. Chem. Phys.* **28**, 608 (1958); [b] I. Fischer-Hjalmars, *Tetrahedron* **19**, 1805 (1963); [c] G. Casalone, C. Mariani, A. Mugnoli and M. Simonetta, *Mol. Phys.* **15**, 339 (1968); [d] M. J. S. Dewar and A. J. Harget, *Proc. Roy. Soc.* **A315**, 443 (1970).
[15]O. Bastiansen and M. Traetteberg, *Tetrahedron* **17**, 147 (1962).
[16a] G. B. Robertson, *Nature* **191**, 593 (1961); [b] A. Hargreaves and S. H. Rizvi, *Acta Cryst.* **15**, 365 (1962); [c] J. Trotter, *Acta Cryst.* **14**, 1135 (1961).
[17]A. Almenningen, O. Bastiansen and P. N. Skancke, *Acta Chem. Scand.* **12**, 1215 (1958); see Ref. 15.
[18]Y. Badar, Chua Cheung King Ling, A. S. Cooke and M. M. Harris, *J. Chem. Soc.* 1543 (1965).
[19]K. A. Kerr and J. M. Robertson, *Ibid.* (B) 1146 (1969).
[20]R. J. W. Le Fèvre, A. Sundaram and K. M. S. Sundaram, *Ibid.* 3180 (1963).
[21]H. Akimoto, T. Shioiri, Y. Iitaka and S. Yamada, *Tetrahedron Letters* **97** (1968).
[22]A. K. Colter and L. M. Clemens, *J. Phys. Chem.* **68**, 651 (1964).
[23]R. E. Carter and L. Melander, *Adv. Phys. Org. Chem.* **10**, 1 (1973).