Theoretical Determination of the Ground State Geometry of 1.3.5-Triphenylbenzene

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The geometry and electronic structure of 1.3.5-triphenylbenzene (TPB) has been determined by semiempirical quantum methods. Using the MNDO approach, the salient dependencies of the first ionization potential, the intramolecular distances and the bond angles on the dihedral angle between the planes of the TPB benzene rings were established. By an application of the CNDO/S method the UV spectrum of TPB was calculated. A comparison of the calculated transition energies with the values observed in the absorption spectrum yields 45° for the dihedral angle, which is in reasonable agreement with the available experimental data.

One of the most considerable efforts in recent physicochemical studies has been towards the determination of the geometry of large organic molecules. In the case of TPB there exist both theoretical and experimental treatments [1 – 6]. The geometry of TPB has been determined experimentally in crystal phase [1], solutions [2, 3] and vapour [4], and theoretically by means of the force field method [5] and the Hückel formalism [6]. Since there exists a great family of more advanced methods (PCILO, MINDO/3, MNDO), which appeared to be capable of predicting the geometry and other molecular properties quite accurately [7 – 9], it seemed to be interesting to use one of them to calculate the geometry of TPB. Central to these methods is the MNDO method, and it was chosen as the most reliable one. However, the overestimation of the torsional angles in flexible molecules by this method being well-established [10 – 11], the dihedral angle between the peripheral benzene rings and the central ring (angle φ in Fig. 1) was determined indirectly: The electronic excitation energies were calculated by the CNDO/S method for several values of this angle. During these calculations all the bond lengths and angles were kept unchanged as obtained by MNDO. Then the transition energies have been compared with those retrieved from the UV spectrum of TPB. A similar procedure for the twist angles of benzylideneaniline was reported to be quite successful [12].

Computational Method

The MNDO program was taken from the QCPE library [13]. Standard parametrization was used [9] and D_3 symmetry was assumed for the TPB molecule. All the geometry parameters were optimized except for the dihedral angle φ (Fig. 1), which was varied between 0 and 90 degrees, every 5 degrees.

The CNDO/S calculation was carried out for each MNDO optimized structure. The parameters of Ellis et al. [14] were used in connection with Mataga-Nishimoto electron repulsion integrals [15]. After SCF iterations a CI procedure within the 100 lowest lying singly excited configurations was performed.

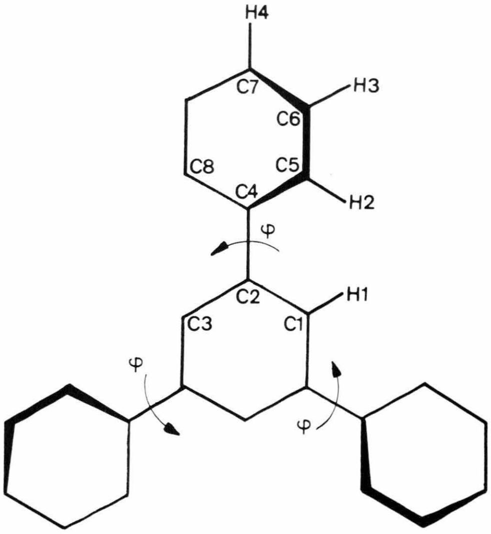

Fig. 1. The TPB molecule.

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Results and Discussion

The MNDO results are presented in Table 1. The minimum of the heat of formation of 95.32 kcal/mol corresponds to the twist angle of 80.0 degrees. Whereas the calculated heat of formation is in fairly good agreement with the experimental value of 90.02 kcal/mol [16, 17], the calculated dihedral angle of the pivot bond of the branched rings is greatly overestimated. Several experimental measurements of this angle have been published. For the gas phase it was found that the value of this angle is in the range of (46 ± 5) degrees [4]. For carbon tetrachloride solutions of TPB the values are close to 35 degrees [2], while in dioxane it was found that they are in the range of (30 ± 10) degrees [3]. The last values were determined from Kerr constant measurements. In the crystal phase the measured angles were 39.2, 35.9 and 34.8 degrees [1]. A value of 41.5 degrees corresponding to $\Delta H = 89.6$ kcal/mol was computed by Allinger with molecular mechanics technique [5], whereas the method of additive increments [18] provided $\Delta H = 88.0$ kcal/mol. Overestimation of the torsional angles in flexible molecules is a typical shortcoming of the MNDO method [10, 11]. This arises from overestimation of the core repulsion integrals which results also in too high heats of formation.

Since all the geometry parameters were kept to be optimized within the assumed D_3 symmetry, it was possible to examine how the strain due to sterical hindrance is distributed over the TPB molecule. The van der Waals interaction between the hydrogen atoms H1 and H2 causes changes mainly in the central benzene ring and in the C4-C5-H2 part of molecular skeleton. The central benzene ring is a distorted hexagon, so the distance from the centre of that ring to the carbon atom C2 is greater than that to C1. At the same time the angles C5-C4-C8 and C4-C5-H2 are smaller than 120.0 degrees. There are no serious distortions of the benzene rings from planarity.

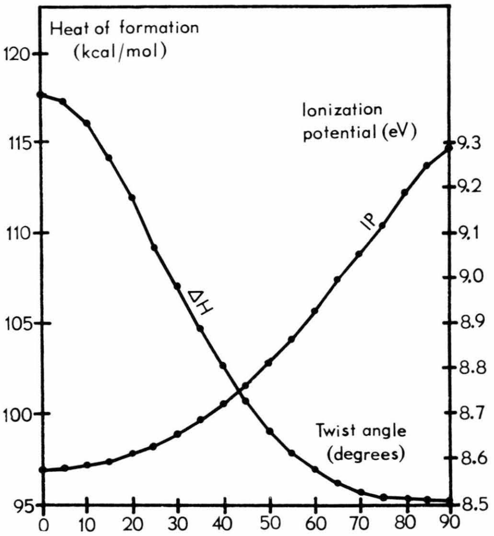

Fig. 2. The MNDO calculated heat of formation and first ionization potential vs. the dihedral angle φ.

Table 1. The MNDO results for TPB[a].

Dihedral angle [degrees]	Heat of formation [kcal/mol]	First ionization potential [eV]	Bond lengths [Å]					Bond angles [degrees]			
			C1-C2	C1-H1	C2-C4	C4-C5	C6-C7	C3-C2-C1	C5-C4-C8	C4-C5-C6	C4-C5-H2
0	117.69	8.577	1.417	1.089	1.493	1.422	1.406	116.5	115.6	122.3	116.2
10	116.11	8.586	1.417	1.090	1.492	1.422	1.406	116.7	116.0	122.1	116.4
20	112.04	8.612	1.417	1.091	1.491	1.421	1.406	117.0	116.3	121.9	116.9
30	107.10	8.659	1.416	1.091	1.489	1.420	1.406	117.5	116.8	121.7	117.5
40	102.59	8.727	1.416	1.092	1.488	1.418	1.405	118.0	117.4	121.4	118.0
50	99.12	8.818	1.414	1.092	1.487	1.417	1.404	118.3	117.9	121.1	118.5
60	96.93	8.929	1.413	1.092	1.487	1.416	1.404	118.5	118.1	121.0	118.7
70	95.67	9.055	1.413	1.092	1.487	1.415	1.404	118.7	118.3	120.9	118.8
80	95.32	9.194	1.413	1.092	1.487	1.415	1.403	118.9	118.5	120.8	118.9
90	95.35	9.289	1.413	1.092	1.487	1.415	1.403	119.0	118.6	120.7	119.1

[a] See Fig. 1; all the other geometry parameters are found to be almost independent of the dihedral angle φ.
This group of parameters includes: bond lengths C7-H4 1.090 [Å], C5-C6 1.405 – 1.406 [Å], C5-H2 1.091 [Å], C6-H3 1.091 [Å]; bond angle C5-C6-C7 119.9 – 120.0 [degrees].
All the torsional angles other than dihedral angle φ (C5-C4-C2-C1) are found to be lower than 1 degree.

The first ionization potential was also calculated by the MNDO method. However, there are no experimental data for the ionization potential of TPB in the gas phase, the only available value IP = 6.00 eV refers to boric acid glass medium [19]. One should expect good agreement between the calculated (8.75 eV for $\varphi = 45°$) and estimated (8.40 eV) ionization potentials, taking into account the fact that the difference between IP's in the gas phase and the boric acid glass is in the order of 2.40 eV.

The question arises about the energy difference between the non-planar three-bladed propeller conformation and the planar form of the TPB molecule (Fig. 2). MNDO favours the non-planar form by 22.3 kcal/mol. The reported value based on molecular mechanics considerations is 12.25 kcal/mol [5] and seems to be more reasonable. There are no experimental data for this quantity.

The ultraviolet spectrum of TPB consists of two broad bands located at 39700 cm^{-1} ($\varepsilon = 51000$) and at 48900 cm^{-1} ($\varepsilon = 57000$), respectively [20, 21]. One can also easily find out that a deflection in the absorption curve appears at about 33500 cm^{-1}. Unfortunately, no calculation for this UV spectrum has been reported up to now. However, the rather successful interpretation of the biphenyl UV spectrum within the CNDO/S framework [22] allows us to expect quite good results of much the same treatment in the case of TPB. Both the orbital energies (Fig. 3) and the calculated excitation energies (Fig. 4) are found to change quite rapidly with the angle φ. The HOMO and HOMO-1 orbitals, which are almost degenerate for $\varphi = 90°$, become splitted by 0.9 eV for $\varphi = 0°$. Similar effects can be observed for the LUMO and LUMO+1 orbitals. The HOMO-LUMO energy gap is reduced from 8.83 eV to 7.29 eV, going from the perpendicular to the planar structure of the TPB molecule.

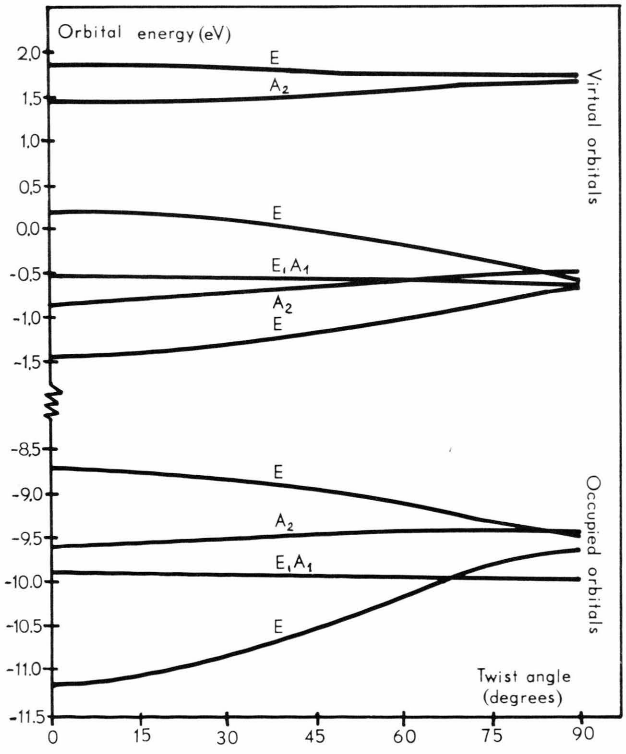

Fig. 3. The CNDO/S calculated orbital energies vs. the angle φ.

The changes of the orbital energies establish the dependence between the angle φ and the excitation energy. While the crude picture of the ordering of the states is retained, all the calculated absorption bands are shifted to the red with decreasing angle φ (Fig. 4). This allows us to estimate the value of this angle by comparing the calculated with the observed transition energy. It was expedient to choose as the reference state, the state with the *E* symmetry, which is attributed in the UV spectrum to the transition centered around 39700 cm^{-1}. The relationship between the number of mixed configurations in the CI procedure and the calculated energy of this state was established in an additional calculation. It was found that the use of 140 singly excited configurations, instead of 100, as used in all the other computations, affects only slightly the energies of the singlet excited states for $\varphi = 45°$. Therefore the latter size of the CI matrix may be considered as sufficient to assign and calculate the absorption bands in the UV spectrum of TPB.

The superimposed condition that the calculated and the observed energy of the chosen reference state should be equal leads to conclusion that the value of the angle φ is close to 45 degrees. This value is to be regarded as reasonable, taking into account the above referred experimental results and the good reproduction of the whole UV spectrum (Fig. 4, Table 2).

The transition to the first singlet excited state of A_2 symmetry, arising mainly from HOMO → LUMO excitation, is very weak and shows as a deflection in the absorption curve at about 33500 cm^{-1} (calculated 33700 cm^{-1}). According to the CNDO/S calcula-

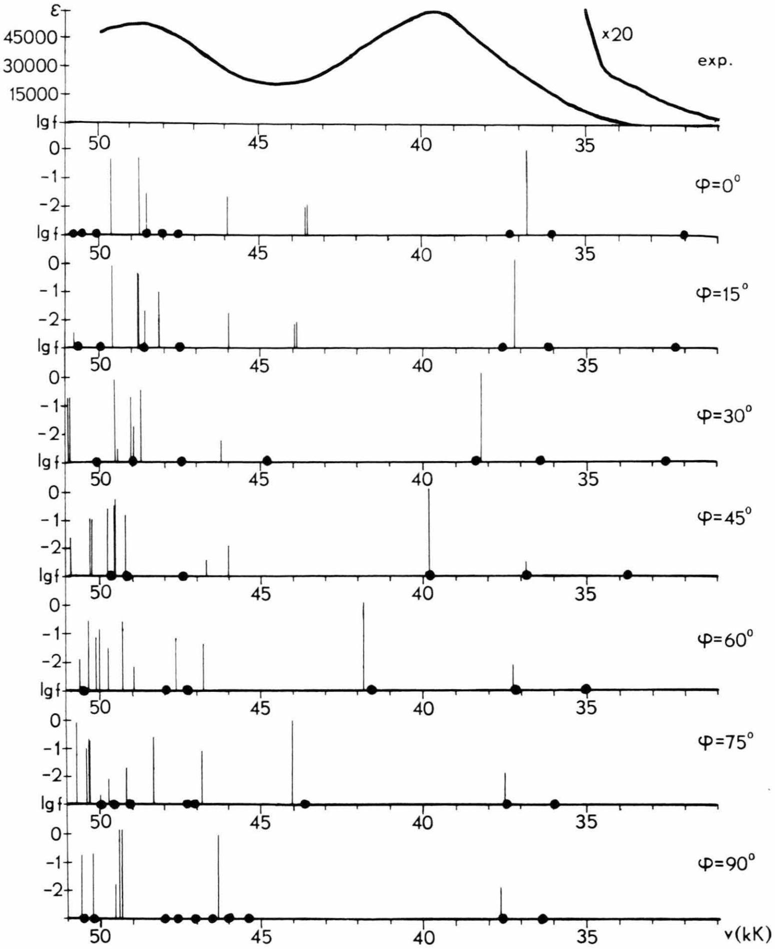

Fig. 4. The comparison between the observed UV spectrum of TPB and the CNDO/S calculated transition energies. Solid points denote the transitions for which the oscillator strength is lower than 1.0E-3.

Table 2. Comparison between the observed and calculated UV spectrum of TPB.

Theoretical values			Experimental results[a]	
Transition energy [cm^{-1}] and symmetry		Oscillator strength	Transition energy [cm^{-1}]	Oscillator strength
33761	A_2	7.3E-5 (z)	33500	–
36805	E	4.9E-4 (x, y)		
36831	A_2	3.5E-3 (z)	39700	1.21
39773	A_1	forbidden		
39805	E	1.32 (x, y)		
45983	E	1.2E-2 (x, y)		
46690	E	3.5E-3 (x, y)	43800[b]	0.20[b]
47405	A_1	forbidden		
49107	A_2	1.1E-4 (z)		
49146	A_1	forbidden		
49200	E	0.145 (x, y)		
49525	A_2	0.578 (z)	48900	1.25
49560	E	0.295 (x, y)		
49621	A_1	forbidden		
49758	E	0.253 (x, y)		
50250	E	0.115 (x, y)		

[a] The transition energies and oscillator strengths were found by fitting a sum of three Gauss functions to the observed spectrum.

[b] Unobserved directly – these values are restored by the afore-mentioned fitting procedure and therefore can be uncertain.

tions, the absorption bands related to the transitions to successive three states have the energies of 36800, 36830 and 39770 cm^{-1} and are hidden under the very strong band attributed to the transition to the afore-mentioned E reference state. For $\varphi = 45$ degrees the calculated and observed excitation energies for this state are 39800 and 39700 cm^{-1}, respectively. The absorption band observed at 48900 cm^{-1} arises from various transitions located theorectically over the range (49190 ÷ 50290) cm^{-1}.

It is well-recognized that the CNDO/S method is a good predictor of ionization potentials when the calculated orbital energies are scaled according to the formula $IP = 0.74\,E_{orb} + 1.70$ [23]. Hence in the case of TPB we obtain the value of 8.30 eV (for $\varphi = 45°$), which seems to be quite reasonable.

1.3.5-triphenylbenzene is one of the larger molecules for which SCF+CI-1 calculations, on the CNDO approximation level, have been carried out. The described approach of determining the twist angles seems to be promising for studies of the geometry of flexible molecules. It may be especially useful when the considered molecule has two or more chromophores connected by single bonds.

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