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Conformational Analysis of Terphenyls by Photoelectron Spectroscopy

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Vapor phase HeI photoelectron spectra of *o*- and *m*-terphenyl were measured, and conformational analysis of biphenyl, *o*-, *m*-, and *p*-terphenyl was made by comparing the observed photoelectron spectral patterns with the calculated ones by the CNDO/S method, the inter-ring twist angles in these compounds being estimated to be around 40°, 60°, 40°, and 40°, respectively. The result that the inter-ring twist angles in *o*-terphenyl are far smaller than 90° is completely in contrast to the long believed perpendicular model of *o*-terphenyl suggested by the gas electron diffraction study.

Concerning experimental studies of molecular conformations of terphenyls in the vapor phases, there has been only one research about *o*-terphenyl by Karle and Brockway1) so far as we know. They studied the molecular structure of *o*-terphenyl by the gas electron diffraction (ED) method, concluding that the inter-ring twist angles θ about the apparently single CC bonds are 90°, and this result has long been believed. However, if their result be correct, it will be unusually interesting because in the case of (*Z*)-stilbene, which is structurally close to *o*-terphenyl, the two phenyl rings are twisted by only 43.2° from the central olefinic group plane according to the recent gas ED study.2)

In this paper we study the conformation of *o*-terphenyl in the vapor phase from the standpoint of photoelectron (PE) spectroscopy to see if Karle and Brockway's result is reasonable. At the same time *m*- and *p*-terphenyl, the conformations of which have not been studied in the vapor phase as yet, are also treated here. This study forms a part of our program to investigate molecular conformations by PE spectroscopy,3) and may present a typical example of the conformational analysis of rather large free molecules by PE spectroscopy.

Concerning the PE spectra of terphenyls, Dewar and Goodman4) reported formerly the ionization energy (IE) values of *o*-, *m*-, and *p*-terphenyl with a low resolution instrument, and Hino *et al.*,[5] the PE spectrum of *p*-terphenyl by a high resolution instrument.

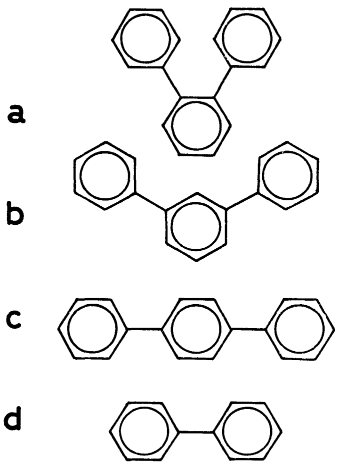

Fig. 1. Structural formulae of (a) *o*-, (b) *m*-, (c) *p*-terphenyl, and (d) biphenyl.

Experimental

Materials. Commercially available *o*- and *m*-terphenyl were recrystallized from methanol and ethanol, respectively, just before use.

Spectroscopic Measurements. Vapor phase HeI PE spectra of *o*- and *m*-terphenyl were measured with the PE spectrometer described formerly.6) The sample inlet and target chamber systems were heated and kept at 104° for *o*-terphenyl and 105° for *m*-terphenyl by circulating hot silicone oil. Xe gas was used as the internal reference for the calibrations of the energy scale.

Computational

CNDO/S7) calculations of biphenyl, *o*-, *m*-, and *p*-terphenyl were carried out on a FACOM 230-75 computer at the Institute of Physical and Chemical Research. All the atomic integral and parameter values necessary for the CNDO/S calculations were taken from or estimated according to Ref. 7.

In the calculations, all the benzene rings of the compounds treated here were assumed to be regular hexagons. In the case of biphenyl, the inter-ring CC single bond length was taken to be 1.489 Å and the CC bond lengths of the benzene rings, 1.396 Å according to the gas ED study.8) All the CH bond lengths of biphenyl were assumed to be 1.0845 Å based on the gas ED data of benzene.9)

Concerning *o*-terphenyl, Aikawa *et al.*10) reported the molecular structural data in the crystalline state by X-ray diffraction (XD) and Brown and Levy,11) by neutron diffraction (ND). In the present calculations, we used the averaged CC and CH bond lengths based on the data by ND, that is, the inter-ring CC bond lengths were assumed to be 1.487 Å, the benzene ring CC bond lengths, 1.390 Å, and the CH bond lengths, 1.090 Å.

In the calculations of *m*- and *p*-terphenyl, the CC and CH bond length values were assumed to be the same as those used in the calculations of biphenyl.

The CNDO/S calculations were carried out for various conformations of biphenyl and the terphenyls, the θ values being changed at intervals of 15° mostly. In the calculations the two phenyl rings in each terphenyl were twisted by the same angle.

Results and Discussion

Photoelectron Spectra. The PE spectra of *o*- and *m*-terphenyl are shown in Fig. 2 and the vertical IEs of these compounds obtained from these spectra are summarized in Table 1 with those of the related compounds.5,12—15) The high resolution PE spectrum of

Table 1. Vertical ionization energies (E_{iv}) of terphenyls and related compounds

Compound	E_{iv}/eV					
o-Terphenyl	8.20	8.7	9.1[a]	9.5[a]	10.9	
m-Terphenyl	8.14	8.5	9.10	9.6	9.8	11.0
p-Terphenyl[b]	8.20	9.17	10.10	11.2		
Biphenyl[c]	8.32	9.05	9.15	9.80	11.20	
Toluene[d]	8.85	9.34	11.43			
o-Xylene[e]	8.57	9.10	11.18			
m-Xylene[f]	8.55	9.03				
p-Xylene[f]	8.43	9.14				

a) An apparent band maximum. b) Ref. 5. c) Ref. 12. d) Ref. 13. e) Ref. 14. f) Ref. 15.

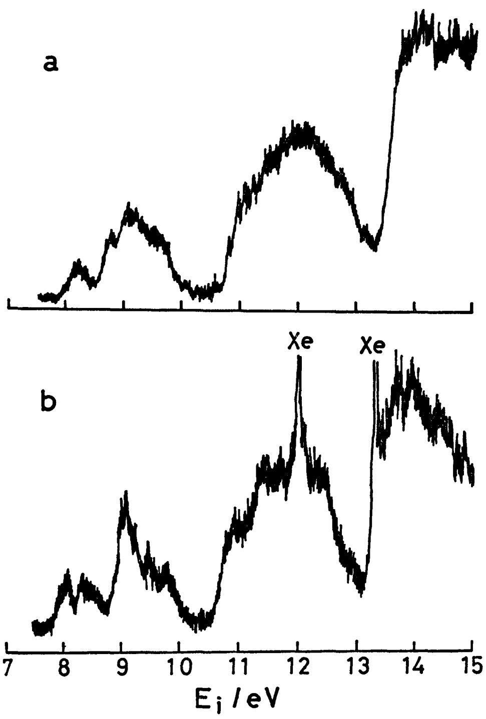

Fig. 2. Vapor phase HeI photoelectron spectra of (a) o-terphenyl and (b) m-terphenyl.

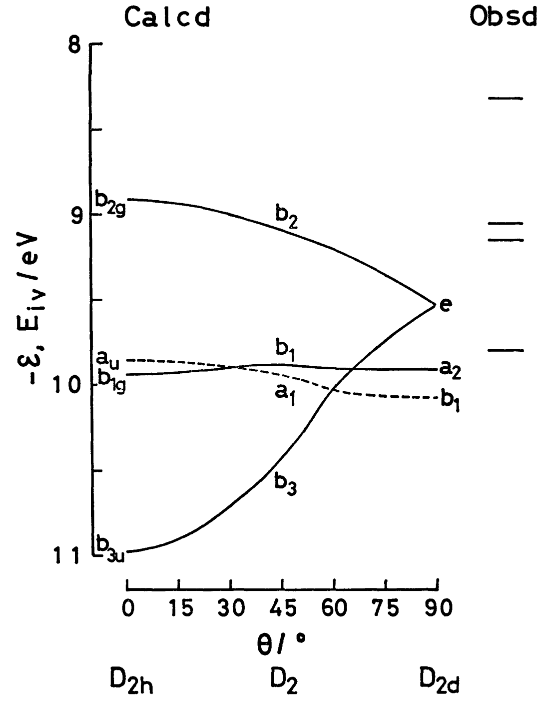

Fig. 3. Calculated orbital energy (ε) diagram with observed vertical ionization energies (E_{iv}) of biphenyl. The z-axis was taken along the long molecular axis.

p-terphenyl was formerly reported by Hino and coworkers.[5] In contrast to the simple pattern of the lower IE part of the PE spectrum of p-terphenyl, the lower energy part of the PE spectrum of o-terphenyl is highly complicated and the spectrum of m-terphenyl is regarded to be the intermediate case. Now we use these PE spectral patterns for the conformational analysis of the terphenyls by comparing the spectral patterns calculated by the CNDO/S method.

Conformational Analysis. *Biphenyl*: At first we examine the validity of the PE spectroscopic method for conformational analysis, which we are now going to use, in the case of biphenyl, as this compound is structurally very close to the terphenyls. The θ value of biphenyl in the vapor phase is (41.6±2)° according to the gas ED study,[8] while this compound is essentially planar in the solid state.[16]

The PE spectrum of biphenyl shows four bands in the IE region from 7.5 eV to 10.5 eV, the second and third bands overlapping highly with each other, and these four bands correspond to the ionizations from the four HO-π-MOs formed by the interactions between the totally four e_{1g}-like π orbitals of the two benzene rings mainly.[12]

In Fig. 3 is shown the orbital energy diagram calculated by the CNDO/S method with the observed vertical IEs of biphenyl. If we compare the vertical IE difference between the first and fourth PE spectral bands with the calculated energy difference between the first and fourth HO-π-MOs, we get 39.3° as the estimated θ value for biphenyl in the vapor. This estimated θ value coincides almost perfectly with the observed one in the vapor by the ED method,[8] that is, in the case of biphenyl the calculated energy difference between the first and fourth HO-π-MOs can directly be compared with the observed splitting between the corresponding PE bands without any corrections in order to estimate the θ value. The similar situation was experienced also in the case of stilbenes[3d] closely related to terphenyls.

Concerning the absolute values of the first four IEs of biphenyl, the CNDO/S calculation for θ=39.3°

predicts the IE values slightly higher (by *ca.* 0.8 eV) than the observed ones commonly, if we assume the validity of the Koopmans theorem,[17] though the intervals between the four bands are well predicted by the calculation.

The vertical IEs of the perpendicular type conformer of biphenyl with $\theta=90°$ are estimated to be 9.534 eV for the first e band, 9.906 eV for the second a_2 band, and 10.082 eV for the third b_1 band by using the CNDO/S orbital energies on the basis of the Koopmans theorem. The predicted splitting of the second and third bands of this conformer is due to a spiroconjugation.[18] By using the first two vertical IEs of toluene,[13] the e band IE of the perpendicular conformer is estimated to be 8.85 eV and the a_2 and b_1 band IEs, 9.34 eV, the spiroconjugation being neglected. That is, in the case of the perpendicular conformer also, the calculation seems to predict slightly higher (by 0.7 eV) IEs, but the difference between the first IE and the averaged IE of the second and third bands predicted by the CNDO/S calculation is 0.46 eV and this value is very close to the estimated one by using the experimental IEs of toluene, 0.49 eV. So far as the IE difference or orbital energy differences are concerned, the calculated orbital energy diagram seems to be realistic over a wide range of θ in the case of biphenyl.

As terphenyls are structurally close to biphenyl and stilbenes, now we may safely apply the same method as used for biphenyl to evaluate the θ values in the terphenyls.

p-*Terphenyl*: At first let us treat the simplest case, *p*-terphenyl. The PE spectrum of *p*-terphenyl shows three bands in the IE region from 7.5 eV to 10.5 eV with the intensity ratio 1:4:1.[5] Similarly to the case of biphenyl, in this energy region totally six bands are expected to appear, corresponding to the six HO-π-MOs formed by the interactions between the six e_{1g}-like π orbitals of the three benzene rings mainly. Therefore, the first and third bands are regarded to correspond to the ionizations from the first and sixth HO-π-MOs, respectively, judging from the above intensity ratio.[5]

In Fig. 4 is shown the orbital energy diagram for the D_{2h} and C_{2h} conformers calculated by the CNDO/S method with the observed vertical IEs[5] for *p*-terphenyl. The energy diagram for the D_{2h} and D_2 conformers is also similar to Fig. 4. By comparing the observed splitting between the first and apparently third PE spectral bands with the energy difference between the first and sixth HO-π-MOs just as in the case of biphenyl, we get 43° as the θ values of *p*-terphenyl if we assume the C_{2h} conformer and 42°, the D_2 conformer. That is, *p*-terphenyl is twisted in the vapor as biphenyl in the vapor, though the θ values of *p*-terphenyl were observed to be 0.4° in the room-temperature stable monoclinic crystal (space group, $P2_1/a$) by the XD and ND methods,[19a] and 15.2°, 18.2°, 23.4°, and 26.8° in the low-temperature stable crystal (space group, $P\bar{1}$) by XD.[19b]

Suzuki[20] estimated the θ values of *p*-terphenyl in solution by the HMO level consideration using the electronic absorption spectra and got 9.5—12.5°. These values do not seem to contradict ours, if we note the point that in the case of biphenyl the θ value was estimated to be 40—43° for the vapor phase and 19—26° for the solution phase by his method.[21] If we estimate the θ value ranges of biphenyl and *p*-terphenyl by using the van der Waals radii,[22] we get the result, $\theta \geq 43°$. The value 43° is very close to the observed θ value of biphenyl in the vapor and those of *p*-terphenyl estimated just now. The reasonable result obtained here for *p*-terphenyl strongly supports the validity of the extended application of the method of conformational analysis tested in the case of biphenyl to the case of terphenyls.

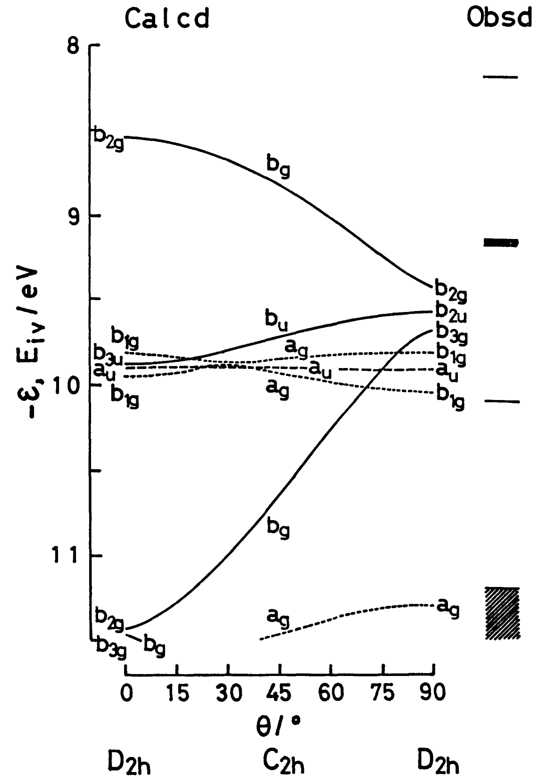

Fig. 4. Calculated orbital energy (ε) diagram with observed vertical ionization energies (E_{iv}) of *p*-terphenyl. The calculated results shown are for the D_{2h} and C_{2h} conformers. The *z*-axis was taken along the long molecular axis.

The first and third PE spectral bands of *p*-terphenyl with the twist angles around 43° are ascribed to the ionizations from the two π orbitals delocalized completely over the entire carbon framework. In the case of *p*-terphenyl also the CNDO/S calculations predict the first six IE values slightly higher (by 0.6—0.8 eV) than the observed ones, though the intervals between the calculated ones are reasonable.

m-*Terphenyl*: Now we move to the slightly more complicated case, *m*-terphenyl. In this case, the PE spectrum shows apparently five bands in the energy region from 7.5 eV to 10.5 eV, the third band being stronger than the others. As in this energy region totally six PE spectral bands are expected to appear in the case of *m*-terphenyl also as in the case of *p*-terphenyl, the third band is regarded to be composed

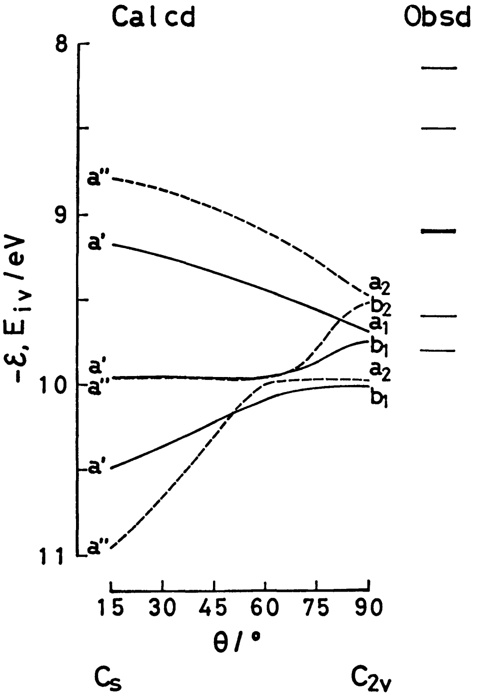

Fig. 5. Calculated orbital energy (ε) diagram with observed vertical ionization energies (E_{iv}) of *m*-terphenyl. The calculated results shown are for the C_{2v} and C_s conformers.

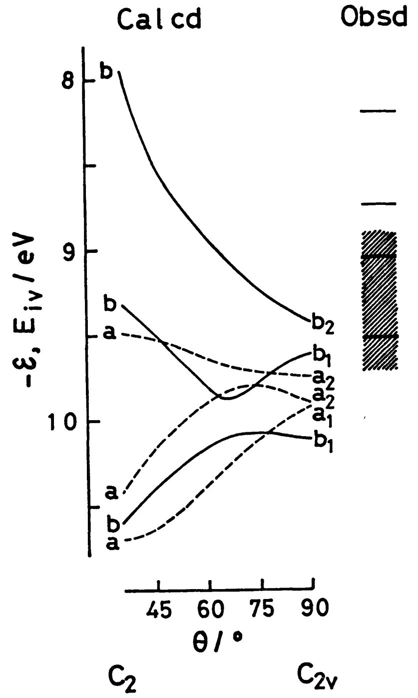

Fig. 6. Calculated orbital energy (ε) diagram with observed vertical ionization energies (E_{iv}) of *o*-terphenyl. The calculated results shown are for the C_{2v} and C_2 conformers.

of two bands overlapping highly with one another.

In Fig. 5 is shown the orbital energy diagram for the C_{2v} and C_s conformers calculated by the CNDO/S method with the observed vertical IEs for *m*-terphenyl. Just as in the case of *p*-terphenyl, by comparing the observed energy splitting between the first and apparently fifth PE spectral bands with the energy difference between the first and sixth HO-π-MOs calculated by the CNDO/S method, we get 35° as the θ values of *m*-terphenyl on the assumption of the C_s conformer and 38°, the C_2 conformer.

The θ value ranges for *m*-terphenyl are estimated to be $\theta \geq 43°$ by using the van der Waals radii,[22] and this value 43° is rather close to those estimated from the PE spectrum here. There have been no gas phase structural data about *m*-terphenyl, but the θ values of 1,3,5-triphenylbenzene closely related to *m*-terphenyl are $(46\pm5)°$ according to the gas ED study by Bastiansen.[23] According to the XD study by Farag[24] the θ values of 1,3,5-triphenylbenzene are $(34\pm2)°$, $(-27\pm2)°$, and $(24\pm2)°$ in the solid state. Recently Busing[25] estimated the θ values in an isolated 1,3,5-triphenylbenzene molecule to be 43.6° using the intramolecular potential function empirically determined from the crystalline data. These literature values for 1,3,5-triphenylbenzene are all consistent with our result for *m*-terphenyl by the PE spectroscopic method.

The calculated orbital sequence of the six HO-π-MOs of *m*-terphenyl is the same as that predicted by the simple HMO model around the twist angles estimated here. The first, second, fifth, and sixth HO-π-MOs are delocalized over the three benzene rings, the third and fourth ones being localized on the two *m*-phenyl groups. The CNDO/S calculations predict IEs slightly higher (by 0.7—0.9 eV) than the observed vertical ones for the first six IEs in the case of *m*-terphenyl also, but the calculated intervals between these six IEs are reasonable. Now the first apparently five bands of *m*-terphenyl are assigned to the a″ (a), a′ (b), overlapping a′ (b) and a″ (a), a′ (b), and a″ (a) bands from the top, respectively, for the C_s (C_2) conformer, the apparently third band being ascribed to the two highly overlapping bands.

o-*Terphenyl*: Now we may safely be able to treat our primary object, *o*-terphenyl, the most complicated one of the three terphenyls. The PE spectrum of *o*-terphenyl shows apparently four band maxima in the energy region from 7.5 eV to 10.5 eV. The first band is isolated from the following band group, their intensity ratio being approximately 1:5. As in this energy region totally six π bands are expected to appear in the case of *o*-terphenyl also just as in the case of *m*- and *p*-terphenyl, the first band is reasonably ascribed to the ionization from only the first HO-π-MO. As the 8.7 eV peak is also weak relative to the 9.1 and 9.5 eV apparent band maxima, the 8.7 eV peak may correspond to one ionization band, and each of the following two apparent strong band maxima may correspond to two overlapping bands. Keeping these points in mind let us carry out the conformational analysis of *o*-terphenyl.

In Fig. 6 is shown the orbital energy diagram calculated by the CNDO/S method for the C_{2v} and C_2 conformers of *o*-terphenyl with the observed vertical IEs. By comparing the observed energy difference between the first and the apparently fourth PE spectral bands with the calculated energy difference between the first and sixth HO-π-MOs, we get 63° as the θ values of *o*-terphenyl on the assumption of the C_2 conformer and 66°, the C_s conformer. The θ value ranges estimated from the van der Waals radii are $\theta \geq 63°$ for the C_2 conformer and $\theta \geq 80°$ for the C_s conformer of *o*-terphenyl, and, therefore, we regard 63° for the C_2 conformer as the most probable θ values of *o*-terphenyl. These values are far from 90° determined by the gas ED method formerly,[1] and rather very close to those observed by the XD[10] and ND[11] methods for the solid states.

Suzuki estimated the θ values of *o*-terphenyl in solution as 42.5—43° by the electronic absorption spectroscopic method,[20] and these values do not contradict ours, if we remember the results for biphenyl mentioned just before in the discussion of *p*-terphenyl. Busing estimated the θ values in an isolated *o*-terphenyl molecule as 54.3° by the intramolecular potential function method.[25] These values are close to ours.

From the discussion given above, the θ values in *o*-terphenyl are around 60° in the vapor phase and at least far from 90°.

The calculated spectral pattern of *o*-terphenyl for the C_2 conformer around $\theta = 63°$ based on the Koopmans theorem[17] reproduces well the overall feature of the observed one though the former is slightly shifted (by 0.6—0.9 eV) to the higher IE side relative to the latter. The orbital sequence of the fifth and sixth HOMOs predicted by the CNDO/S method is reversed to that predicted by the simple HMO model. In the case of *o*-terphenyl as in the case of (*Z*)-stilbene[26] the overlap integrals between the two twisted *o*-phenyl ring group π orbitals are not negligible and through-space orbital interactions between these orbitals, which are taken into account in the CNDO calculations automatically, may influence the orbital orderings. However, further detailed discussions about the orbital orderings of *o*-terphenyl are hindered by the highly overlapping nature of the PE spectral bands. Now the first apparently three bands of *o*-terphenyl are ascribed from the top, respectively, to the b, a, and overlapping b and a bands followed by the overlapping b and a bands corresponding to the fourth apparent band maximum for the C_2 conformer.

Summary of θ Values by Various Methods. Finally the θ values in the terphenyls and related compounds given by various methods for various phases are summarized in Table 2 for the sake of comparison. Le Fèvre *et al.*[27] estimated the θ values of the terphenyls and 1,3,5-triphenylbenzene in solution phases based on the molecular polarizability data or molar Kerr constants as given in Table 2. Their results are qualitatively consistent with ours. Recently Wakayama[28] estimated the θ values of *p*-terphenyl in solution at 77 K to be larger than 16° from its $S_1 \leftarrow S_0$ absorption in solution compared with that of crystalline state at 77 K on the basis of the XD data by Baudour *et al.*[19b] Theoretically Gamba *et al.*[29,30] calculated the θ values of biphenyl and the terphenyls by the molecules-in-molecule method by taking into account the non-bonded interactions, and their theoretical values are consistent with our present results.

Table 2. Inter-ring twist angles(θ) in terphenyls and related compounds

Compound	θ/°									
	PES[a]	EAS[b]		ED[c]	XD[d]	ND[e]	MP[f]	IMP[g]	MIM[h]	VDWR[i]
	(gas)	(gas)	(solution)	(gas)	(solid)	(solid)	(solution)	(free molecule)		
o-Terphenyl	63(C_2) 66(C_s)		42.5—43[k]	90[l]	42.5[o] 62.1	42.1[t] 62.1	55(C_2)	54.3	55[u]	≥63(C_2) ≥80(C_s)
m-Terphenyl	38(C_2) 35(C_s)						20		37[u]	≥43
p-Terphenyl	42(D_2) 43(C_{2h})		9.5—12.5[k]		0.4[p] 15.2[q] 18.2 23.4 26.8		20		37[u]	≥43
Biphenyl	39.3	40—43[j]	19—26[j]	41.6±2[m]	0[r]				40[v]	≥43
1,3,5-Triphenylbenzene				46±5[n]	34±2[s] −27±2 24±2		38	43.6		≥43

a) This work by gas phase HeI photoelectron spectroscopy combined with CNDO/S calculations. Assumed molecular symmetries are given in parentheses after θ values. The error ranges for θ values are estimated to be several degrees from the result for biphenyl. b) Electronic absorption spectra treated on the HMO level. c) Gas electron diffraction. d) X-ray diffraction. e) Neutron diffraction. f) Molecular polarizability approach based on molar Kerr constants, Ref. 27. g) Empirical intramolecular potential function approach, Ref. 25. h) Molecules-in-molecule approach taking into account non-bonded interactions. i) This work using the van der Waals radii. j) Ref. 21. k) Ref. 20. l) Ref. 1. m) Ref. 8. n) Ref. 23. o) Ref. 10. p) At room temperature, Ref. 19a. q) At 113 K, Ref. 19b. r) Ref. 16. s) Ref. 24. t) Ref. 11. u) Ref. 29. v) Ref. 30.

Conclusion

Summing up the discussion given above it is concluded that *o*-terphenyl is more twisted than biphenyl, *m*- and *p*-terphenyl, but the inter-ring twist angles in *o*-terphenyl are around 60° and far from 90° in the vapor phase in contrast to the former gas ED result. It has been demonstrated that PE spectroscopy is very useful for the conformational analysis of rather large molecules in the vapor phase to which the other methods such as the gas ED method and the microwave spectroscopic method are not so easy to be applied.

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