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A CONFORMATIONAL STUDY OF PHENYL- AND NAPHTHYL-NAPHTHALENES

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Abstract—The energies of 1-phenyl-naphthalene, 2-phenyl-naphthalene, 1-(1′-naphthyl-)naphthalene, 1-(2′-naphthyl-)naphthalene, and 2-(2′-naphthyl-)naphthalene have been calculated as a function of the twist angle. The total energy was obtained as a sum of the π-electron energy, nonbonded interactions and the energy of stretching for the inter-ring bond. For the most interesting conformations, the positions and the intensities of the first electronic bands have been calculated by the MIM method, and compared with experimental spectra. The possibility of using the spectroscopic results in conformational analysis is discussed.

INTRODUCTION

IN THE last few years, considerable efforts have been made to elucidate the conformation of molecules by means of *semi* empirical calculations based largely on Westheimer's method.[1-8] A number of calculations have been performed for the molecule of biphenyl both in vapour[9-11] and crystalline phase.[8] A similar approach has been used in the present paper to investigate the ground-state equilibrium conformations for phenyl- and naphthyl-naphthalenes. Since UV absorption spectra have been extensively used to establish the conformation of molecules of this type,[10, 12-15] a calculation of transition energies and oscillator strengths for the first few bands of these molecules, in different conformations, has been carried out to check the sensitivity and the reliability of this technique.

METHOD

For each molecule, the potential energy curve, as a function of the twist angle (θ), has been obtained superposing on the Hückel π-electron energy curve, the non-bonded interaction curve, and the stretching energy for the C—C bond connecting the two aromatic fragments.

The ideal geometry assumed had regular hexagonal benzene and naphthalene rings with bond-lengths equal to 1·40 Å. The inter-ring bond was varied in the range 1·44–1·52 Å. Twist angles from 0° to 180° (or 90° for summetrical cases) were considered with a scanning of 15°. All C atoms were taken in sp^2 hybridization and the C—H bond-lengths was 1·08 Å.

The standard Hückel technique was used with $\beta_0 = -20$ Kcal/mole. For the inter-ring bond, β was taken dependent from bond-length and twist angle as follows:

$$\beta = \beta \frac{S}{S_0} \qquad (1)$$

where S and S_0 are the overlap integrals on Slater orbitals. The non-bonded interactions have been evaluated with Bartell's functions.[16] All inter-ring H···H, H···C, and C · · · C interactions have been included. The stretching energy for σ component of the inter-ring bond has been calculated by the formula:

$$E_s = 0{\cdot}5\ k_s\ (r - r_e)^2 \qquad (2)$$

where $k_s = 2303{\cdot}5$ Kcal/(mole Å^2) and $r_e = 1{\cdot}483$ Å.[8]

The electronic transitions have been calculated using the "Molecules in Molecules" method (MIM). Recently this method, developed by Longuet–Higgins and Murrell[17] to interpret the spectra of compounds in which the conjugation between the component fragments in a molecule is negligible, has been extensively extended both to rigid conjugated hydrocarbons[18] and homoconjugated chromophores.[19] When the necessary data are available, this procedure has been recognized[18] to need much less computational work, especially for large molecules, and to lead to more satisfactory results, than the commonly used Pariser–Parr–Pople method.[20]

For this reason MIM method has been applied here to the substituted naphthalenes. Naphthalene and benzene, respectively, are the component fragments for the related molecules; the procedure and the parameters used to calculate transition energies are the same as in Ref. 18.

Transition intensities were calculated according the known relation:

$$f = 1{\cdot}085\ 10^{11}\nu\lambda^2 \qquad (3)$$

RESULTS AND DISCUSSION

Since the curve of total energy as a function of the twist angle θ for the ground state of all molecules at different inter-ring bond lengths have shown that the twist angle corresponding to the energy minimum is independent of the inter-ring distance (an example is shown in Fig. A), energy curves *versus* inter-ring distance at constant θ have been drawn (Fig. B). Since for all molecules it appears that the distance of minimum energy is at about 1·49 Å, and the curves of the type shown in Fig. 1 never cross, only the results obtained at a distance of 1·49 Å will be shown from now on.

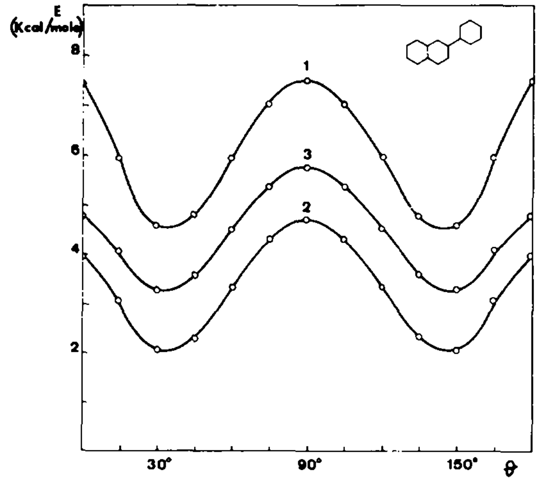

FIG. A Total energy *vs* twist angle curves for 2-phenyl-naphthalene. (1) = 1·44 Å, (2) = 1·48 Å, (3) = 1·52 Å for the inter-ring distance, respectively.

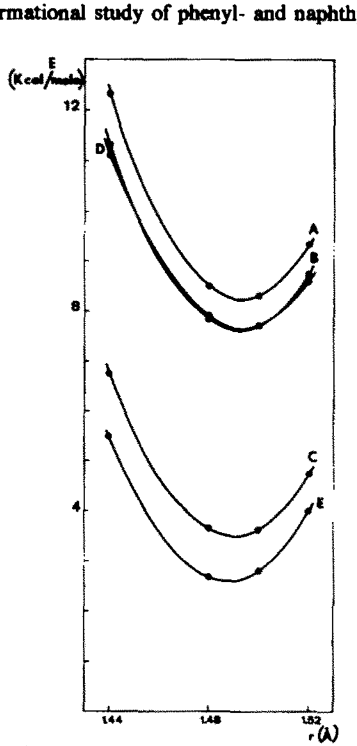

FIG. B Energy curves *vs* inter-ring distance.

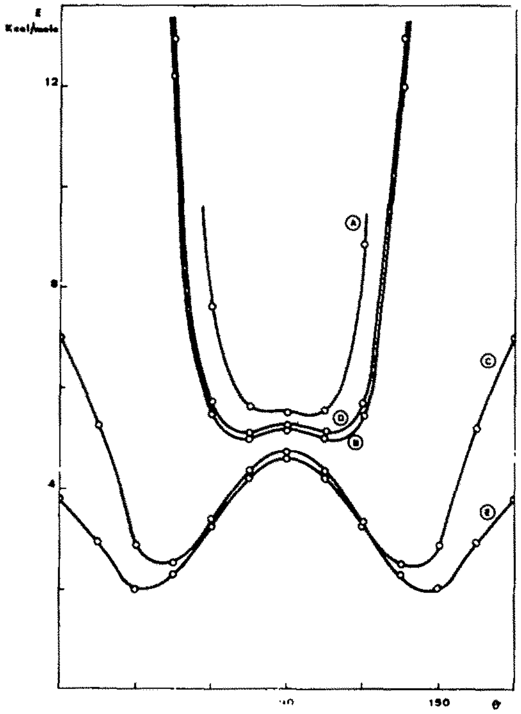

FIG. 1 Total energy *vs* twist angle curves. π electron energy calculated by Hückel method. (A = 1-(1,-naphthyl-)naphthalene; B = 1-(2,-naphthyl-)naphthalene: C = 2-(2- naphthyl-)-naphthalene; D = 1-phenyl-naphthalene; E = 2-phenyl-naphthalene).

It can be seen that the curves for 2-phenylnaphthalene and 2-(2,-naphthyl-) naphthalene show two minima at about 30° and 150°, while 1-phenylnaphthalene, 1-(1,-naphthyl-)naphthalene, and 1-(2,-naphthyl-)naphthalene curves have a rather flat region of low energy between 60° and 120°. As expected in 1-substituted compounds, the two rings are nearly planar. Experimental evidence in this direction for 1-(1,-naphthyl-)naphthalene has been given.[22]

The variation of the ground state π electron energy as a function of the twist angle obtained by Hückel method is well correlated with the same quantity obtained by the MIM method. By means of this correlation the total energy curves shown in Fig. 2 were obtained. It can be seen that the positions of minima are practically unchanged.

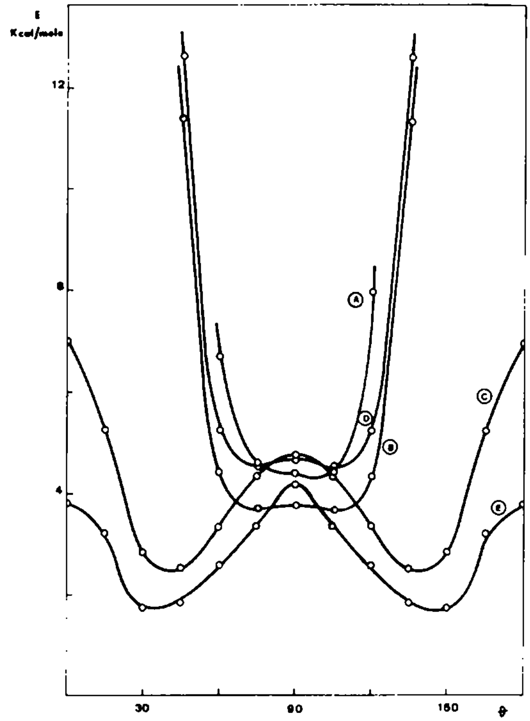

Fig. 2. Total energy *vs* twist angle curves. π electron energy claculated by MIM method.

The position and intensity of the first bands in the spectrum of each molecule have been calculated for θ equal to 0°, 90°, and for two other values of θ close to the values of the energy minima. The results are shown in Table 1, where also experimental values are reported.[23,24]

At twist angles corresponding to the energy minimum, the agreement between experimental and theoretical spectra is as good as can be expected for calculations of this kind. It is clear that spectroscopic results and particularly the position of the first band can be confidently used to distinguish between molecules with angle of twist nearly zero or nearly 90°. This can be seen in the cast of phenylnaphthalenes as shown in Fig. 3. However the assessment of an angle of twist on the basis of the spectrum is very doubtfull and hazardous, since, for angles of twist close to those predicted to correspond to energy minima by our comformational analysis, the calculated spectra are almost independent from the twist angle.

TABLE 1. MAIN TRANSITION ENERGIES AND OSCILLATOR STRENGTHS (f > 0·1).

ΔE(exp)	f	ΔE	f	ΔE	f	ΔE	f	ΔE	f
A		$\theta = 0°$		$\theta = 75°$		$\theta = 90°$		$\theta = 105°$	
		−0·219	—	−0·015	—	0·000	—	−0·015	—
3·90(24)	0·02	3·227	0·80	3·830	0·82	3·943	0·99	3·821	0·80
4·22	0·25	4·498	0·02	4·297	0·20	4·752	0·04	4·273	0·20
		4·699	0·73	4·711	0·06	5·086	0·11	4·786	0·04
		5·070	0·08	5·100	0·11	5·581	1·08	5·041	0·13
5·48	0·80	5·206	0·08	5·495	0·56	5·587	2·05	5·445	0·82
		5·405	0·78	5·525	0·62	5·811	0·99	5·498	0·37
		6·059	2·99	5·624	0·33	6·420	0·93	5·598	0·70
		6·413	1·20	5·706	0·04			5·623	0·63
		6·687	0·16	5·744	0·51			5·886	1·52
				6·414	0·56			6·414	0·91
				6·440	0·42			6·718	0·06
B		$\theta = 0°$		$\theta = 70°$		$\theta = 90°$		$\theta = 110°$	
		−0·208	—	−0·025	—	0·000	—	−0·025	—
4·05(24)	0·42	3·651	0·95	4·135	1·14	4·250	1·38	4·123	1·09
		4·284	0·37	4·409	0·37	4·511	0·48	4·438	0·42
		4·810	0·35	4·650	0·34	5·123	0·16	4·631	0·37
5·00	0·20	5·100	0·41	5·127	0·17	5·295	0·01	5·099	0·19
		5·264	0·38	5·297	0·05	5·467	1·76	5·508	1·19
5·50	1·42	5·426	0·12	5·552	1·29	5·943	1·68	5·589	0·16
5·70	1·68	5·567	0·29	5·583	0·37	6·459	0·60	5·813	0·28
		5·976	1·61	5·833	0·52			6·014	1·85
		6·032	0·34	5·938	1·07			6·449	0·58
		6·546	0·96	6·477	0·66			6·710	0·03
		6·744	0·17	6·730	0·06				
C		$\theta = 0°$		$\theta = 35°$		$\theta = 90°$		$\theta = 145°$	
		−0·235	—	−0·136	—	0·000	—	−0·136	
4·50(24)	0·80	3·872	0·33	4·021	0·80	4·481	0·80	3·921	0·40
		4·406	0·12	4·434	0·12	4·530	0·43	4·565	0·82
4·90	1·30	4·826	0·20	4·856	2·63	4·947	3·07	4·831	2·86
		4·923	5·26	4·929	0·78	5·290	0·10	4·897	0·07
		5·267	0·22	5·590	0·29	6·117	0·88	5·497	0·12
5·83	0·60	5·648	0·63	5·708	0·06	6·411	0·64	5·749	0·28
		5·693	0·52	5·898	0·28	6·806	0·05	5·901	0·28
		5·925	0·26	6·209	0·10			6·335	1·28
		6·239	1·08	6·501	1·30			6·336	0·12
		6·525	0·75						
		6·810	0·20						

D		$\theta = 0°$		$\theta = 70° = 110°$		$\theta = 90°$	
		−0·235	—	−0·044	—	0·000	—
4·22(23)	0·20	3·497	0·74	3·843	0·25	4·302	0·87
		4·207	0·18	4·264	0·61		
5·48	1·04	5·431	1·61	5·311	0·10	5·600	2·02
				5·576	1·88		
5·83	0·40	5·654	0·11				
		6·099	0·11				
6·66	1·20	6·384	0·74	6·393	0·87	6·397	0·91
		6·623	0·29				
		6·763	1·20	6·766	1·22	6·760	1·13

E		$\theta = 0°$		$\theta = 30° = 150°$		$\theta = 90°$	
		−0·220	—	−0·168	—	0·000	—
3·88(23)	0·01	3·904	0·06				
		3·930	0·62	4·022	0·60		
4·33	0·24	4·493	0·22	4·500	0·28	4·509	0·55
4·97	0·90	5·106	1·65	5·110	1·55	5·182	2·39
		5·221	0·28	5·221	0·47	5·299	0·08
		5·644	0·14	5·646	0·13		
5·81	0·70	6·192	0·21	6·140	0·18	5·980	0·25
		6·401	0·65	6·393	0·62	6·404	0·70

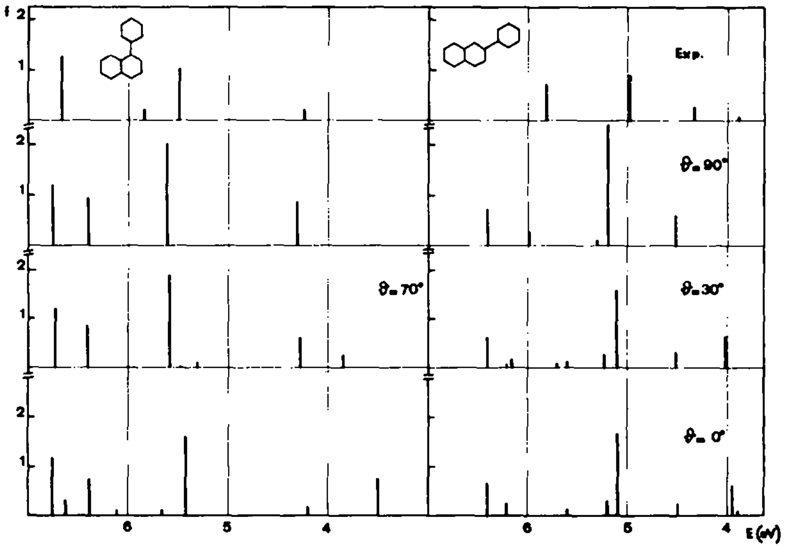

FIG. 3 Experimental (23) and calculated spectra for D and E molecules.

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